ADMET DEPOLYMERIZATION: THE SYNTHESIS OF PERFECTLY DIFUNCTIONAL TELECHELICS

By

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This dissertation is dedicated to the very special women in my life:
my grandmothers, my mother, my sister, and my wife, all of whom have given me the confidence to succeed at whatever I attempt.

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The synthesis of perfectly difunctional telechelics via acyclic diene metathesis (ADMET) depolymerization is presented. ADMET depolymerization chemistry offers an efficient route in recycling high molecular weight polymer to perfectly difunctional telechelics. This chemistry is only possible when Lewis acid free metathesis catalysts of the type, M=CHR(N-2,6-C_6H_3-*i*-Pr_2)$(OCMe(CF_3)_2)_2$ (M = W or Mo), are employed.

The use of functionalized depolymerizing agents has proven to be a viable route in the formation of a variety of α,ω-terminated telechelics. Tungsten and molybdenum versions of Schrock's catalyst were employed in the depolymerization of 1,4-polybutadiene with allyltrimethylsilane. Schrock's molybdenum catalyst synthesized α,ω-bis(trimethylsilyl)-1,4-polybutadiene (n = 1 and 2), whereas the tungsten version produced the same telechelic with n = 2,

3, and 4. Due to the molybdenum catalyst's high efficiency, it became the catalyst of choice in ADMET depolymerization, and was used when allylchlorodimethylsilane quantitatively depolymerized 1,4-polybutadiene to α,ω-bis(chlorodimethylsilyl)-octa-2,6-diene.

The negative neighboring group effect limits the synthesis of telechelic esters and silyl ethers, whereby at least two methylene spacers must separate the olefin from the respective functionality. However, allylphthalimide can be used as a depolymerizing agent even though the nitrogen is β to the olefin. Apparently, coordination of the imide is minimized, thereby allowing quantitative conversion of polybutadiene to the imide functionalized telechelic.

Through this experimentation, the depolymerization mechanism was elucidated whereby the reaction initially forms macrocyclic butadienes which then ring-open to generate telechelics. With this knowledge, a new reaction scheme has been developed, and has enabled us to synthesize tailored molecular weight telechelics.

The depolymerization of butyl rubber and polyisoprene have proven to be more difficult than that of 1,4-polybutadiene, due to the fact that the depolymerization of butyl rubber and polyisoprene must proceed through a tetrasubstituted metallocycle. From ^{1}H NMR analysis, it appears that the problem in the depolymerization of polyisoprene lies in the inability of the sterically hindered olefins to form the tetrasubstituted metallocycle.

CHAPTER 1

INTRODUCTION

Synthesis of perfectly difunctional telechelics has been a challenge for many years. This dissertation addresses this challenge and demonstrates the synthesis of telechelics with a functionality of 2.0 via acyclic diene metathesis (ADMET) depolymerization. Also presented herein is the elucidation of the ADMET depolymerization mechanism, which provides a reaction scheme to synthesize tailored molecular weight telechelics. This chapter introduces previous methodologies used in the formation of telechelics, develops an understanding of olefin metathesis, and shows how metathesis chemistry can be used in polymer degradation and the synthesis of telechelics.

Definition and Applications of "Telechelics"

The term "telechelic polymer" was first coined by Uraneck *et al.*[1] to describe low molecular weight macromolecules possessing two reactive functional groups situated at both chain ends. The term originates from the Greek words *telos* (far), and *chelos* (claw), thus describing two claws on opposing ends of the molecule which are able to grab (react with) other molecules.

Of course the use of prepolymers as monomers is not a new concept. As early as 1937, Otto Bayer recognized the potential of this chemistry in the synthesis of polyurethanes, whereby hydroxy-terminated prepolymers were

reacted with diisocyanates.[2] The use of varied molecular weight hydroxy prepolymers enabled chemists to produce materials with a broad range of physical properties due to their different polymer architecture.

Telechelics are inherently interesting because they can be employed as comonomers to generate block copolymers, crosslinking agents in the formation of networks, and chain extenders in the linking of small chains to form large chains.[3]

Over the years the term telechelic has broadened in its definition. Originally telechelics were defined as difunctional prepolymers, whereby the functionalities were selectively reacted with other molecules. Now, the term telechelic has been expanded to polymers with one or more functionalities, and are defined as monotelechelic, tritelechelic, tetratelechelic, and polytelechelic. Since the general definition of telechelic is a difunctional polymer, a molecule with one functionalized end group can also be termed semitelechelic. Depending on the desired application of the telechelic, a certain degree of functionality is synthesized. In most cases, however, the desired functionality is approached or exceeded but never obtained. Herein lies the challenge of synthesizing perfectly difunctional molecules.

Almost all synthetic methods have been used to generate difunctional telechelics, i.e., stepwise polymerization, free radical polymerization, anionic polymerization, cationic polymerization, ring opening polymerization and degradation of polymers. Most of these techniques have approached or exceeded 2.0 functionality, and thus have never obtained perfect difunctionality.

Perfect difunctionality is important. When telechelics are used as comonomers in the synthesis of block copolymers, a stoichiometric balance of endgroups is necessary if high polymer are to be generated. Stated another

way, if stoichiometric imbalance occurs the polymerization will only proceed to oligomers.

Synthesis of Telechelics Via Step-Growth Polymerization

Step growth polymerization has been very limited in the formation of telechelics, despite the fact that this process can utilize all known organic reactions to form macromolecules. To generate high polymer, greater than 99% reaction conversion must be obtained. Unfortunately, there are few organic reactions that proceed without side reactions, thereby limiting the synthesis of difunctional telechelics by this methodology.

Step growth polymerization is the only viable route in producing telechelic polyamides and polyimides, which have important applications due to their high thermal stability. Published results from step growth polymerization of polyamides and polyimides are not characterized sufficiently to calculate a degree of functionality, though a high degree of functionality is not imperative for the crosslinking applications in which these telechelics are used.

In most cases, there must be a stoichiometric balance of monomers to form high molecular weight polymers via step polymerization. On the other hand, Stille *et al.*[4-7] and others[8-12] found that a stoichiometric imbalance could be efficiently employed to form telechelics. To limit the degree of polymerization, Stille[4] used an excess of 4,4'-diamino-3,3'-di-benzoyldiphenyl ether with 4,4'-diacetyldiphenyl ether to form oligomers terminated by the functionality in excess (Figure 1.1). This is shown in the following relationship: $DP = (1 + r) / (1 + r - 2rp)$ where r = stoichiometric imbalance ($monomer_1/monomer_2$), p = reaction conversion, and DP = degree of polymerization. For example, when r = .9308 and p = .99, the DP = 22.

In Figure 1.1, the telechelic polyquinoline is chemically modified to the desired biphenylene terminated telechelic for crosslinking purposes. As stated before, the degree of functionality in biphenylene telechelics is not vital in its role as a crosslinking agent since greater than 99 % conversion is not needed. The reported degree of functionality would therefore rule out the possibility of using such telechelics in copolymerizations or grafting reactions.

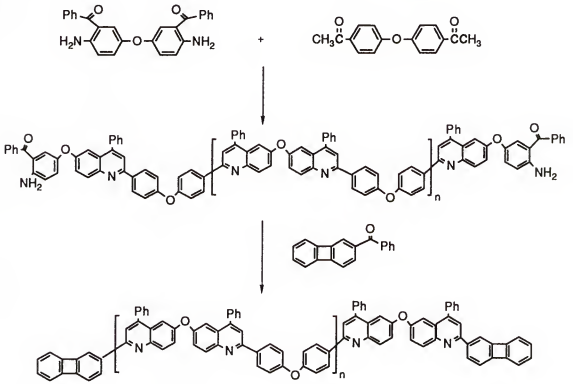


Figure 1.1. Synthesis of α,ω-bis(biphenylene)polyquinoline.

While stoichiometric imbalance is the preferred method of producing telechelics by step-growth polymerization, the use of a chain limitator has also been successful. In chain limitation, a monofunctional compound is reacted *in situ* with difunctional monomers, resulting in a telechelic terminated by the monofunctional compound. As shown in Figure 1.2, hydroxyl-terminated telechelic carbonates were synthesized by this method.[13] The molecular

weight of the telechelic was controlled by the molar concentration of the monofunctional compound, where the theoretical degree of polymerization is X_n = 2/X; X being the molar ratio of monofunctional reactant to monomer.

Futhermore, as illustrated in Figure 1.2, a percentage of the phenolic groups of bisphenol A are protected prior to the addition of phosgene. After the reaction reached completion, the protecting group was removed to form α,ω-bis(hydroxy)polycarbonate. Although there was a very good fit between the experimental and theoretical molecular weights, the evidence provided for the degree of functionality still was inconclusive.

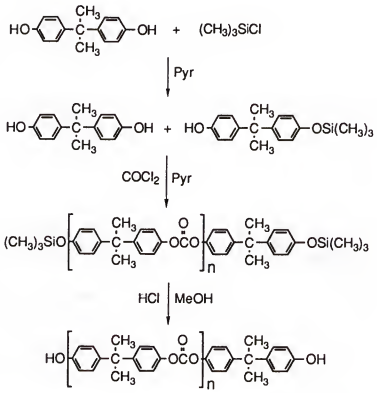


Figure 1.2. Synthesis of α,ω-(hydroxy)polycarbonate by chain limiting step polymerization.

It is evident that step polymerization is an important method in preparing thermally stable rigid telechelics, since these compounds are unable to be

prepared using other methods. Unfortunately, there are many side reactions which occur during step polymerization of both high polymers and telechelics, which limit the scope of the reactions. This is why telechelics are usually synthesized using radical or ionic methodologies.

Synthesis of Telechelics Via Anionic Polymerization

The ability to synthesize predetermined molecular weight polymers with low polydispersities was developed in living anionic polymerization.[14] The term "living" is used to describe the propagating anionic species reacted in a system void of chain termination and chain transfer. To form difunctional telechelics by living anionic polymerization, a functionalized initiator is introduced at the α-position while the ω-position is terminated by the corresponding functionality of the initiator.

Under ideal conditions, each molecule of initiator consumed translates into one polymer chain. The molecular weight of the chains then can be calculated by the following equation: $M_n = M/I$, where M = weight of monomer and I = moles of initiator. As a result, the "living" nature of the polymer allows for the generation of tailored molecular weight telechelics.

Monomers employed in anionic polymerization must have an electron deficient double bond in which the propagating anion attacks. Examples of the most common vinyl and dienyl monomers that may be polymerized anionically are styrene, α-methyl styrene, butadiene, isoprene, and methyl methacrylate.[15]

In the anionic polymerization of both butadiene and isoprene, the solvent employed affects the microstructure of the polymers. In hydrocarbon solvents, the propagating anion is insoluble and exists as a σ complexed contact ion pair.[16] For instance, in the polymerization of butadiene, the propagating

polybutadienyl species has a negative charge on the terminal carbon (I) which ensures that the terminal carbon is incorporated into the backbone of the polymer. Hence, high degree of 1,4 microstructure is obtained (Figure 1.3).



I II

Figure 1.3. Polybutadienyl anions in hydrocarbon (I) and polar solvents (II).

In polar solvents, the solvated ion pair forms a π-allyl complex (II) in which comparable electron density presides at the 2- and 4-carbon atoms. Thus, the probability that propagation will occur at the 2-position is enhanced and results in increased 1,2 addition.[16]

Nonpolar solvents must be employed to form well defined polymer structures with a negligible amount of 1,2 addition. For example, polymerization of butadiene in hexane generates a polymer with 92% 1,4 microstructure.[17] On the other hand, the polymerization of butadiene in THF results in a polymer with 96% 1,2 microstructure.[17] As will be discussed, the use of nonpolar solvents causes solubility problems with initiators required for anionic polymerization of telechelics.

There are two types of anionic initiators used in the synthesis of telechelics: dianion initiators[18-21] and blocked functional initiators.[22-27] Dianion initiators have two propagating anions which can be terminated with alcohol, carboxylic acid, or amine functionalities. One disadvantage of dianion initiators is that the association of the living chain ends causes gelation, thereby hindering the attack of the terminating functional group which decreases the

functionality of the telechelic.[21] It has been discovered that the gelation problem is particularly troublesome in nonpolar solvents, which as discussed before, are the solvents of choice in achieving well-defined polymer microstructures.

However, blocked functional initiators have only one propagating anion, thus alleviating the problem of gelation. As shown with dianion initiators, blocked functional initiators have also been limited due to their insolubility in nonpolar solvents. Until recently, only a blocked hydroxyl functional anionic initiator was soluble in benzene,[25] but now a blocked amine functional initiator has been developed which is soluble in nonpolar solvents.[26,27]

An advancement in the synthesis of acrylate and methacrylate telechelics occurred with the discovery of group transfer polymerization.[28] Although not a anionic process, group transfer is a living polymerization which proceeds by way of a Michael addition where the monomer adds to a reactive silyl ketene acetal (Figure 1.4). In the course of each propagation step, the trimethylsilyl group is transferred from the propagating chain end to the incoming monomer unit.

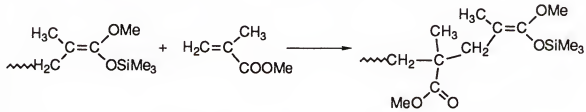


Figure 1.4. Group transfer polymerization of methyl methacrylate.

Unlike anionic polymerization, group transfer polymerization of acrylates can occur at ambient temperature without side reactions. Group transfer polymerization is a living polymerization which produces narrow polydisperse

polymers. These polymerizations use a catalyst, usually a bifluoride compound, in concentrations of less than 1% of the initiator, which does not effect the molecular weight of the polymer. The utility of group transfer polymerization is limited to those monomers which do not contain acidic protons that could cause chain termination.

Since group transfer polymerization is a living polymerization, it allows for the formation of telechelics by blocked functional initiators and/or functional termination. As shown in Figure 1.5, a protected hydroxyl initiator is used in the polymerization of methyl methacrylate, leading to a semitelechelic (III) upon deprotection.[29] The polymerization also can be terminated to form a difunctional hydroxyl telechelic (IV) whereby the two living chain ends are coupled via a difunctional terminator, 1,4-bis(bromomethyl)benzene.[29]

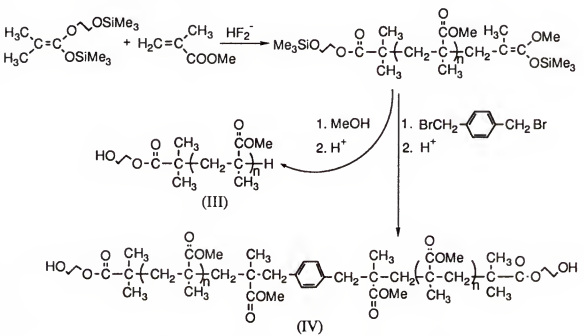


Figure 1.5. Synthesis of mono and ditelechelics via group transfer polymerization.

Both anionic and group transfer polymerizations are living polymerizations which generate well-defined telechelics. Anionic polymerizations afford polymers with narrow polydispersities, and if the problem of gelation is overcome by the employment of blocked initiators, telechelics with a functionality close to 2.0 are synthesized. Even though anionic polymerization generates a high degree of functionality, only a 92% 1,4 microstructure is synthesized. For this reason, other methods must be used to form perfectly linear unsaturated telechelics.

Group transfer polymerization is an efficient method in producing acrylic telechelics with linear polymer backbones, narrow polydispersities, tailored molecular weights, ambient reaction temperatures, and no side reactions. Monofunctional telechelics are synthesized also with great efficiency and are used in the formation of block copolymers.

Synthesis of Telechelics Via Cationic Polymerization

The field of cationic living polymerization remained secondary to anionic living polymerization for approximately 30 years. This is not a surprise because the propagating carbocations are extremely reactive and thus not very selective. In fact, even experimentation under rigorous, high vacuum conditions has yielded non-reproducible results.[30] It was not until 1984, that an approach to truly living cationic polymerization was developed.[31,32]

The first living cationic polymerization was the synthesis of poly(vinyl ethers), initiated by a mixture of HI and I_2.[31,32] The resultant polymer had a narrow polydispersity, and desired molecular weights could be synthesized by controlling the HI to monomer ratio. It was shown experimentally that the concentration of I_2 did not have an effect on the molecular weight of the

polymer. The proposed polymerization mechanism of vinyl ethers, by Iodine and hydrogen iodine initiation, is displayed in Figure 1.6.

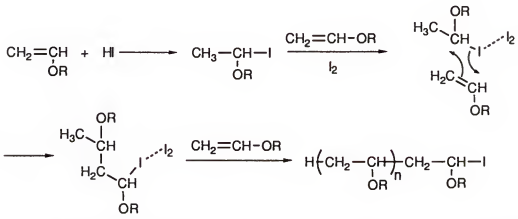


Figure 1.6. Cationic polymerization mechanism of vinyl ethers with HI / I_2 initiation.

The same reaction can be used in the formation of α,ω-diodo vinyl ether telechelics employing the HI / I_2 initiator and α,ω-(divinyloxy)butane monomer (Figure 1.7).[33] Once the diodo telechelics are synthesized, simple organic transformations can produce a plethora of α,ω functionalities.

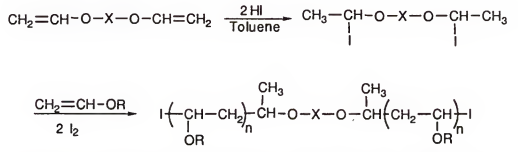


Figure 1.7. Cationic polymerization of telechelic vinyl ethers where X = $(CH_2)_4$.

During the time that the first living carbocationic polymerization of vinyl ethers was discovered, another laboratory was in the process of developing the

first isobutylene polymerization.[34,35] Instead of using similar iodo initiators, a reagent was synthesized which acts as both an initiator and a transfer agent, hence the term "inifer agent". The first bifunctional inifer agent generated was 1,4-*tert*-benzylic chloride. As shown in Figure 1.8, the polymerization is initiated when the inifer agent reacts with BCl_3 forming a carbocation. This carbocation then reacts with isobutylene, and continues to propagate until either termination or transfer occurs. In the transfer step, the propagating carbocation is transferred to the inifer agent forming the more thermodynamically stabilized benzylic carbocation, which in turn initiates propagation (second reaction, Figure 1.8). If termination occurs, the chloro terminated chain end can be activated by BCl_3 generating the initial propagating carbocation. This activation/deactivation process continues until all monomer is consumed and terminated by chlorine. The final product is α,ω-chloro(polyisobutylene) which can be derivatized into a variety of telechelics.[34-37]

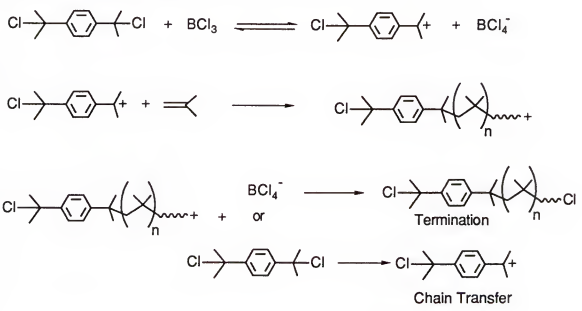


Figure 1.8. Inifer methodology in cationic polymerization.

The framework for living cationic polymerization has been constructed with the discovery of both HI / I_2 initiator and the inifer agent. Now monomers with electron donating functionalities can be polymerized, opening a new frontier in polymer chemistry. Not only are these monomers polymerizable, difunctionalized telechelics can be generated and are presently being used in industrial applications.[37]

Synthesis of Telechelics Via Free Radical Polymerization

There are three main steps in the synthesis of polymers by free radical techniques: initiation, propagation, and termination. For this technique to be valuable in the synthesis of telechelics, all three steps must exclude side reactions.

There are two methods of initiating free radical polymerizations, functional initiators or telogens.[38] The synthetic method in which functional initiators are used is displayed in the classical radical polymerization scheme (Figure 1.9). The initiation step begins with homolytic cleavage to form the primary radical (Figure 1.9). It is important that initiator decomposition occurs in the formation of one primary radical, so that upon polymerization, the telechelic has definitive end groups. For instance, homolytic cleavage of bis acyl initiators can undergo partial decarboxylation and form two separate initiators thereby creating a combination of three possible α,ω telechelics.[39] It is also imperative that initiator and monomer reactivities are comparable. If this is not the case, the initiator will react with the oligomer, causing chain transfer and resulting in the generation of mono and trifunctional telechelics.

Once initiated, the propagating radical can react with monomer, or chain transfer with initiator, oligomer, or solvent. Polymerizing under bulk conditions reduces the amount of chain transfer.

In the termination step, the reaction may proceed by combination or disproportionation. In the case of combinate termination, the propagating radical is terminated with another propagating radical or a primary radical. For the generation of perfectly difunctional telechelics, termination must be recombinant. The other mode of termination is disproportionation, which terminates the growing chain by hydrogen abstraction, causing the functionality to be less than 2.0.

Initiation	$I \rightarrow 2R$
	$R\cdot + M \rightarrow RM\cdot$
Propagation	$RM_n\cdot + M \rightarrow RM_{n+1}\cdot$
Termination	
Combination	$2RM_n\cdot \rightarrow RM_{2n}R$
	$RM_n\cdot + R\cdot \rightarrow RMR$
Disproportionation	$2RM_n\cdot \rightarrow RM_nH + RM_n{=}CH_2$

Figure 1.9. Radical polymerization scheme.

Controlling initiation, propagation, and termination has made free radical polymerization a difficult methodology in synthesizing telechelics. For example, in the polymerization of ethylene, the termination occurs predominantly by combination. This behavior was studied by using linear alkyl radicals to calculate the rates of termination k_d and k_c. According to the calculated rates, one should expect the functionality to be equaled to 1.8.[40] When ethylene is

reacted with AIBN in *t*-butanol, which has a very low transfer constant, a product with a functionality of 1.7 is obtained.[41] The discrepancy in functionality can be attributed to the highly reactive alkyl radicals abstracting hydrogen from the initiator.

Similarly, styrene's termination is 80% combinate. This corresponds to a telechelic which is 80% bifunctional and 20% monofunctional, numbers which translate into a telechelic with a functionality of 1.67, if this is in fact the only reaction controlling the structure of the product.[42,43] In the synthesis of styrene telechelics initiated by AIBN, the formation of telechelics with a functionality close to 2.0 were obtained,[44,45] contrary to the values calculated by termination products. This deviation in functionality is thought to be caused by primary radical termination, which is in higher concentration when low molecular weight telechelics are produced.[42,43]

The initiator of choice in radical polymerization of telechelics is AIBN, which produces α,ω-dinitrile telechelics. If dinitrile end groups are not desired, other functionalities such as diamino, diacid, and diisocyanates can be generated from the nitrile endgroup.[46]

Free radical polymerization of telechelics is still limited to monomers with high degree of termination by combination. For instance, the termination reaction of methyl methacrylate with AIBN is mainly disproportionate;[47] therefore, it can not be used in telechelic applications.

On the other hand, telomerization is not as dependent on combination/ disproportionation reactions. Telomerization reactions differ from functionalized initiators whereby a small concentration of initiator reacts with the transfer agent, a difunctional reagent, to produce a functionalized radical (Figure 1.10). The radical propagates and is terminated upon reaction with a transfer agent. Since the transfer agents have such high reactivity, most telomerizations have

few repeat units before termination occurs. Most successful telomerizations have a low level of stationary radicals which minimize the probability of disproportionate termination. An example of a telomerization reaction is shown in Figure 1.10, whereby a peroxide initiator reacts with the telogen, carbon tetrachloride, and initiates the telomerization.[48] Aliphatic halogen compounds, such as carbon tetrachloride, are readily used in telomerizations of olefins due to their high transfer constants.[49]

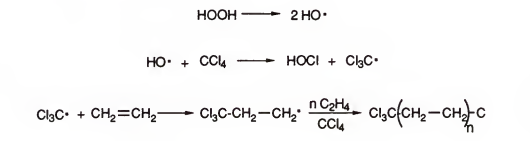


Figure 1.10. Free radical telomerization of ethylene.

Both functionalized initiators and transfer agents are useful in the synthesis of telechelics if and only if side reactions are excluded. It has been shown that many different functionalities can terminate telechelics generated by this methodology. The choice of monomers employed, when functionalized initiators are used, is limited to the monomers which terminate by combination reactions. In telomerization reactions, less emphasis is focused on combination/disproportionation reactions because the highly reactive transfer agent consumes most of the free radicals. The problem with telomerization reactions is that the transfer agent reacts with the propagating monomer before a high degree of polymerization has taken place, and this results in telechelics with very few repeat units. Overall, in well behaved reaction systems, free radical polymerization can produce telechelics with functionalities close to 2.0.

Synthesis of Telechelics Via Ring Opening Polymerization

The synthesis of telechelics via ring-opening polymerization can proceed by two methods, anionic and cationic polymerization. To date the most successful technique has been accomplished by anionic methodology. A primary example is the industrial production of polyether polyols, a monomer in the synthesis of polyurethanes.[50,51] In the synthesis of polyethers, ethylene oxide is initiated by sodium hydroxide and produces a living polymer that is quenched with acid to form the telechelic diol. The formation of the polyethers is enthalpically driven by the release of ring strain. The propagating anion does not participate in chain transfer to polymer thereby making this an efficient route in producing perfectly difunctional telechelics. Most of the anionically ring-opened telechelics do not undergo chain transfer. The exceptions are ε-caprolactone[52] and cyclosiloxane,[53] where polymer-cyclic oligomer equilibria have been observed. In the case of cyclosiloxanes, monofunctional "end blockers" have been reacted with cyclosiloxanes to produce telechelics with known molecular weights. The cyclics that are formed can be removed *in vacuo*, yielding the telechelics (Figure 1.11).[53,54]

On the other hand, the mechanism for cationic ring-opening polymerizations illustrates the susceptibility to chain transfer. The first mechanistic step is the protonation of the cyclic's heteroatom followed by the nucleophilic attack of the monomer at the carbon α to the heteroatom. Analogous to anionic ring-opening polymerization, the driving force is the release of ring strain. However, heteroatoms in the polymer backbone are capable of nucleophilic attack, thereby creating a competition with the polymer chain and monomer to react with the protonated species, thus forming cyclic (I) or branched (II) chains (Figure 1.12).[55]

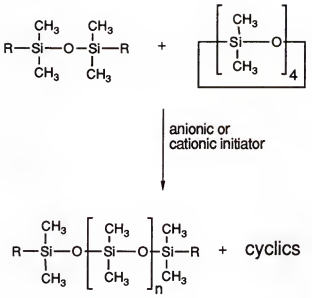


Figure 1.11. Ring-opening polymerization of telechelic siloxanes.

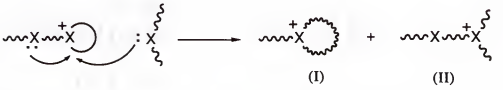


Figure 1.12. Two possible chain transfer reactions in ring-opening polymerization.

Even though there is chain transfer in cationic ring-opening polymerization, telechelics of cyclic ethers,[56,57] sulfides,[58] amines,[59] and acetals[60] have been synthesized in this manner, the most widely studied monomer being THF.[61,62] These telechelics have a functionality greater or less than 2.0 due to chain transfer with polymer.

The utility of ring-opening polymerization in the synthesis of telechelics is limited due to two factors: 1) few monomers are capable of polymerizing by anionic ring-opening polymerization because most carbon-heteroatom bonds do not have enough polarization for nucleophilic attack to occur. Examples of

cyclic compounds that will not undergo anionic ring-opening are cyclic amines, four and five membered ethers, and acetals.[63] 2) Chain transfer reactions cause the degree of functionality to become a number other than two, thereby making it difficult to use these telechelics in further applications. The only known exception is the ring opening polymerization of ethylene oxide which has been a valuable technique in synthesizing perfectly difunctional α,ω-hydroxy(polyethers).

It will be shown in this dissertation that olefin metathesis is a viable route in synthesizing perfectly linear and difunctional telechelic polybutadiene. An introduction to olefin metathesis is presented before the synthesis of telechelics via this methodology is discussed.

Olefin Metathesis

The term olefin metathesis was derived from the Greek words meta (change) and tithemi (place) to describe the interchange of two olefins resulting in the formation of two more olefins. This exchange process was first termed olefin metathesis by Calderon[64] in 1967, and the name has existed ever since. Along with exchange reactions, olefin metathesis can be applied to ring opening polymerization (ROMP) and degradation chemistry (Figure 1.13).

In the early stages of olefin metathesis, two types of catalyst systems were employed depending on the metathesis reaction sought. In the case of ring opening metathesis polymerization, the first open publication disclosed the use of a transition metal based catalyst accompanied by a Lewis acid cocatalyst ($MoCl_5/Et_3Al$) similar to those used in Zieglar-Natta polymerizations.[65] These Zieglar-Natta type catalysts are used at room temperature, whereas the use of supported oxide catalysts, MoO_3/Al_2O_3, are employed at elevated temperatures

and efficiently catalyze disproportionation reactions (exchange reactions).[66] The supported oxide catalysts also have been used in ROMP reactions but result in poor yields of polymer.[67] It was not until the discovery of $WCl_6/EtAlCl_2/EtOH$ that a catalyst was utilized both in ROMP and disproportionation reactions.[68,69] Due to this revelation, a transition metal based catalyst with a Lewis acid cocatalyst would soon be the most studied catalyst/cocatalyst system.

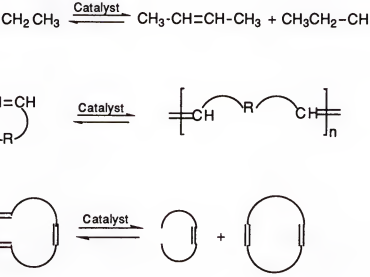


Figure 1.13. Three categories of olefin metathesis: exchange, ROMP, and degradation.

With the development of the new catalyst system, Calderon *et al.*[70] proposed an olefin metathesis mechanism wherein a [2+2] cycloaddition reaction of two olefins was promoted by coordination to the transition metal catalyst (Figure 1.14). This mechanism, which came to be known as the "pairwise mechanism," was well supported by similar known processes which involved a 4-centered transition state and did in fact explain the product mixtures observed.

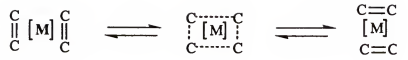


Figure 1.14. Pairwise mechanism.

According to the pairwise mechanism, the cross metathesis reaction of a cyclic olefin and an unsymmetrical olefin, catalyzed by $WOCl_4/Bu_4Sn$ or $WOCl_4/Et_2AlCl$, was predicted to form one product.[71] Instead, a mixture of products was observed which refuted the pairwise mechanism and prompted a metal carbene mechanism to explain the results. In the metal carbene mechanism, initially there must be generation of a propagating carbene, whereby the most probable route to the carbene is the alkylation of the transition metal followed by dehydrohalogenation (Figure 1.15).[72] After the carbene is produced, the catalytic species reacts with an olefin to form a metallacyclobutane that can cleave productively to form a new carbene or degeneratively to form starting materials (Figure 1.16).[71] This exchange is indicative of a reversible process which is determined by a thermodynamic equilibrium.



Figure 1.15. Carbene formation of Zieglar-Natta-type catalyst.

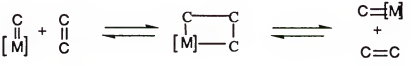


Figure 1.16. Metal carbene mechanism.

Although the metal carbene mechanism is not the only plausible mechanism, it was thought to be the most conclusive due to many informative reactions.[73-75] However, another version of the pairwise mechanism had been proposed, whereby one of the olefins of the cross metathesized product, shown in Figure 1.14, vacates a catalytic site and enables another acyclic olefin to become coordinated to the metal center. This allows for the cross metathesis between the initial olefin (sticky olefin) and the newly coordinated olefin which in turn generates a new pair of olefins. This process is termed the sticky olefin mechanism due to the slow exchange of the olefin in comparison to the rate of metathesis.[76,77]

In principle, the only way to prove that olefin metathesis proceeded through the metal carbene mechanism was to synthesize a preformed carbene and monitor its activity. At that time, Fischer carbenes were the only preformed carbene, but they could not catalyze olefin metathesis.[78] It was not until four years after the carbene mechanism was proposed that a preformed metal carbene exhibited metathesis catalysis.[79]

To further establish the carbene mechanism, two acyclic olefins, butene and octene, were cross metathesized with a cyclic olefin, cyclooctene (Figure 1.17).[73] The product distribution was analyzed as close to the beginning of the reaction as possible and extrapolated to measure the product ratios at time zero. According to theoretical data, if the reaction proceeds via the pairwise or sticky olefin mechanism, the ratio of products (C_{14}/C_{12}) $(C_{14}/C_{16}) = 0$ and 3 respectively. However, the product ratio was experimentally found to be 4.05 ± 0.05, an insignificant difference from the value 4 anticipated according to the metal carbene mechanism. This experiment gave further evidence that olefin metathesis proceeds by a metal carbene mechanism.

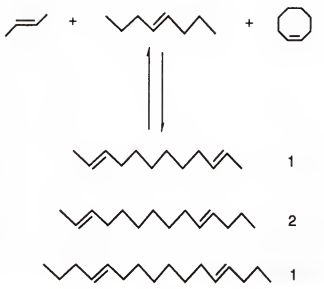


Figure 1.17. Experimental evidence of the carbene mechanism.

As stated earlier, preformed metal carbenes were proven to catalyze olefin metathesis, but it was not until later that the initiation and propagation of a single component metal carbene was identified by ^{1}H and ^{13}C NMR spectroscopy.[80-82] In addition, the intermediate metallocyclobutane adducts were isolated,[83] thereby providing the final proof of the metal carbene mechanism.

Degradation of Unsaturated Polymers by Olefin Metathesis

In the introduction of olefin metathesis, three categories of reactions were briefly mentioned: exchange, ring-opening polymerization, and degradation reactions. While exchange reactions and ring opening polymerizations have been thoroughly studied for many years, the efficient degradation of unsaturated polymers to reusable products i.e. telechelics, is still in its

developmental stages. A major problem with these degradation reactions stems from the fact that classical catalyst system causes side reactions.

There have been two types of degradation reactions via olefin metathesis, these being intramolecular and intermolecular metathesis. Intramolecular metathesis was the first degradation reaction in which polybutadiene, with a high 1,4 microstructure, was catalyzed with WCl_6/EtAlCl2/EtOH to form macrocyclics with the number of repeat units ranging from 3-8 (Figure 1.18).[84] Later, others[85-89] have demonstrated that a variety of metathesis catalysts can be used in analogous intramolecular degradation chemistry.

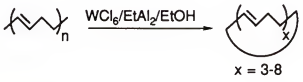


Figure 1.18. Intramolecular metathesis of 1,4-polybutadiene.

Intramolecular degradation can be accelerated when the initial concentration of polymer is below the equilibrium concentration ("equilibrium concentration" is defined as the maximum concentration of polymer at which there is quantitative conversion of linear polymer to macrocyclics). If the concentration of polymer is higher than the equilibrium concentration, the polymer undergoes partial degradation affording macrocyclic oligomers and residual high molecular weight linear polymer. For instance, the equilibrium concentration for polybutadiene in chlorobenzene at 30°C is 0.65 M .[90,91]

The majority of intramolecular degradation reactions have employed polybutadiene, although an alternating poly(isoprene-butadiene) copolymer and polyisoprene degradation have also been attempted. In fact, the copolymer

was successfully degraded to cyclic oligomers (n = 2, 3, 4). The degradation was found to occur at the unsubstituted olefins formed between the butadiene and isoprene repeat units.[92] Attempts to degrade polyisoprene were initially unsuccessful due to a short lived catalyst system.[93] A more stable catalyst system, $W[OCH(CH_2)Cl)_2]_2Cl_4$-$AlEt_2Cl$-anisole, was employed and allowed to react for 10 days, resulting in the degradation of polyisoprene from the molecular weight of 10^6 to approximately 2.0×10^4.[94] Along with the decreased molecular weight, there was a loss of unsaturation caused by cationic side reactions derived from the ill-defined classical catalyst system.

Similar results were reported when the catalyst system tungsten hexachloride and tetramethyl tin were employed in the degradation of polyisoprene.[95] There was a decrease in molecular weight from 10^6 to 10^3, along with a considerable decrease in the vinylic resonances of polyisoprene which can not be explained by metathesis chemistry. One possible explanation for the decrease in unsaturation could be acid catalyzed cyclization, which is well documented for polyisoprene (Figure 1.19).[96-98] One could speculate that the acid was generated from the *in situ* formation of the carbene which proceeds through the aforementioned dehydrohalogenation.

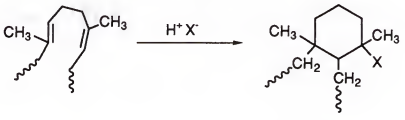


Figure 1.19. Acid catalyzed cyclization of polyisoprene.

Soon after intramolecular degradation was discovered, the first intermolecular metathesis degradation reaction was published, whereby

polybutadiene was cross metathesized with an internal acyclic olefin in the presence of catalyst $WCl_6/EtAl_2$.[99] Since an unsymmetrical acyclic olefin, 2-hexene, was used in the cross metathesis reaction, the reaction afforded oligomers with 1 and 2 repeat units terminated by either methyl or propyl end groups, or one of each. Once degradation via intermolecular cross metathesis was successful, symmetrical olefins were employed to synthesize defined end groups. With known end groups, a prediction of the relative distribution of oligomeric species can be derived from a statistical equation dependent upon the ratios of symmetrical olefin to polymer repeat unit ([Q]/[M]) where Q = half the symmetrical olefin and M = polymer repeat units.[100] If the molecules Q and M are reacted, the oligomeric products would have the following structure: QM_xQ where both halves of the symmetrical olefin terminate the ends of the oligomer. If X_Q and X_M equal the total mole fractions of X_Q = Q/Q+M and X_M = M/M+Q, the mole fraction of QM_xQ containing (x+1) double bonds can be used to derive the following equation:

$$X_{QMxQ} = X_Q^2 X_M^x (x+1) = X_Q^2 (1- X_Q) (x+1)$$

where the summation X_{QMxQ} from x = 0 to infinity is 1.0.[100] This equilibrium distribution function can then be used to predict the mole fractions of the oligomeric species produced in the degradation reactions (X_{QMxQ}). For example, when polybutadiene was degraded with a ratio of [Q]/[M] = 10, three products were found with values of x = 1, 2, and 3.[100] The mole fractions of these products were 83.4, 14.2, and 2.4 respectively, and were in good agreement with the predicted values from the equilibrium function. When [Q]/[M] < 9, the tendency to form macrocyclics is increased and can not be accounted

for in the distribution function; therefore the equation is only valid for large values of [Q]/[M].[100,101]

The kinetics of metathesis degradation are simple if cyclics are neglected in the rate equation, and all double bonds in the polymer react with equal probability so there is a statistical chain scission. The first to describe such a degradation was Kuhn[102] in the hydrolysis of carbohydrates. In large excess of symmetrical olefin, the degradation reaction proceeds by a pseudo-monomolecular reaction to low molecular product

$$A + B \rightarrow 2\,C$$

and is described by the following rate equation; k_1 = rate constant, t = reaction time, s = number of split double bonds / number of original polymer double bonds.[103]

$$-k_1 t = \ln (1-s)$$

In addition, the weight fraction of a product with a given number of repeat units (n) can be calculated at any value of s; w = weight fraction.

$$w_n = n\,s^2\,(1-s)^{n-1}$$

Both the equations presented above were tested against experimental data from the degradation of 1,4-polybutadiene with octene and a good fit was found. In the initial reaction period, there was a small deviation assumed to be caused by the formation of the active catalytic species.[103]

The statistical equations presented herein have ignored the formation of cyclic oligomers when the concentration of symmetrical olefin was relatively large. With smaller concentration of symmetrical olefin, the formation of cyclics initially predominates and quickly reaches a maximum.[104] The formation of macrocyclics takes place by a simple back biting mechanism which is accelerated in dilute conditions and small concentrations of a cross metathesis agent. The ring-chain equilibria has been calculated in the degradation of

poly(pentenylene) by empirical force field calculations, K_{298} = [a] / [b] [c] = 1.30.[105] There has been speculation that the macrocyclics are intermediates of metathesis degradation, but further work must be done to qualify this speculation.[103]

As metathesis degradation evolved, the utility of this process varied from research group to research group. In the case of Hummel *et al.*, polymer degradation by cross metathesis of an acyclic olefin, was used to investigate the structure of unsaturated polymers by analyzing the degraded low molecular weight fragments. It was thought that the clean degradation products were easier to analyze, by gas chromatography/mass spectral techniques, in comparison to the analysis of polymers. This technique has been used successfully to investigate the structure of crosslinked polymers,[106-108] copolymers,[109,110] and chemically modified polymers.[111-113]

Instead of employing strictly hydrocarbon symmetrical olefins, different compounds with heteroatoms were used to form low molecular weight fragments in which the α,ω-positions have reactive endgroups. The formation of telechelics by this method was attempted in the early 1980's and discovered that certain heteroatoms either coordinated or reacted with the catalyst, thereby rendering the catalyst inactive.

Streck[114] wrote an in depth review establishing a quick screening test to see which functionalized olefins would participate as chain transfer agents in the polymerization of poly(pentenylene). If the functionalized olefin was metathetically active, the polymer's viscosity was reduced and the process was easily followed by viscosity measurements. Unsaturated compounds which were found to be ineffective in modifying molecular weights of ring-opening metathesis polymerizations were esters of acrylic acid, esters of methacrylic acids, esters of maleic and fumaric acid, acrylonitrile, and 1,1-dichloroethylene,

to name just a few. On the other hand, active metathesis compounds were esters of unsaturated alcohols, ethers of unsaturated alcohols, and esters of unsaturated carboxylic acid as long as there was no conjugation between the carbonyl and the olefin, alkenyl silanes, and alkenyl stannanes. Since it was just a screening test, analysis was not presented to determine the degree of functionality in these molecules.

Concurrently, an attempt to use dimethyl-3-hexenedioate in the degradation of polybutadiene (M_n=10^5) with WCl_6/Me_4Sn resulted in a polybutadiene prepolymer capped by ester groups (Figure 1.20).[115] According to the patent, only 92 % of the product is ester terminated. The same symmetrical olefin and catalyst was used in the ring-opening polymerization of cyclooctadiene.[116-117] The polymerization technique led to similar results found in degradation chemistry.

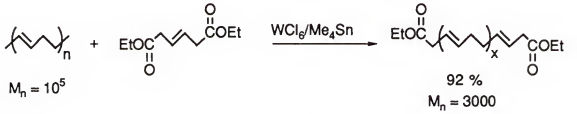


Figure 1.20. Degradation of 1,4-polybutadiene with dimethyl-3-hexenedioate.

These results can be explained by the premise that coordination between the ester and carbene decreases the reactivity of the ester olefin, thereby allowing for the formation of non-functionalized polybutadiene.[117] This technique was further advanced when a diborane symmetrical olefin was used in both polymerization and degradation chemistry in the synthesis of telechelic 1,4-polybutadiene.[118,119] The interest in the borane olefin originated with the idea that the borane would not coordinate with the alkylidene; therefore, the

reactivity of the symmetrical olefin would not decrease. The polymerization generated α,ω-diborane polybutadiene which was oxidized to α,ω-bis(hydroxy)polybutadiene. The degree of functionality was never calculated, but the telechelic was polymerized with caprolactone to produce a high polymer, verifying that the functionality was close to 2.0. The diborane symmetrical olefin also was employed in the degradation of polybutadiene (Figure 1.21). As described above, the products were isolated, oxidized, and reacted with caprolactone. This time only a few connections were made indicating a low degree of functionality.

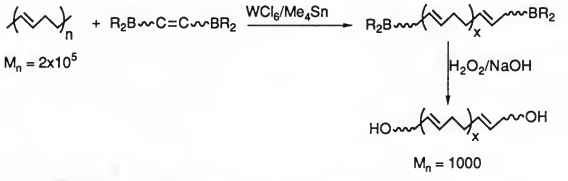


Figure 1.21. Depolymerization of 1,4-polybutadiene with 1,10-bis(9-BBN)-5-decene

The limitations of this chemistry originate from the use of a classical catalyst system ($WCl_6/SnBu_4$) which induces side reactions. Compounds which cause these side reactions can be generated from the formation of the active catalytic species,[95] from decomposition of the catalyst,[103] and from cationic reactions initiated by the Lewis acid cocatalyst *i.e.* vinyl addition.[117]

In order for well defined products to be synthesized, a preformed metal carbene had to be developed with enough activity that a Lewis acid cocatalyst would not be needed. Fischer-type carbenes did not catalytically initiate olefin metathesis.[78] Schrock chronicles his quest for this Lewis acid free alkylidene in

which he set out to synthesize in 1973 and ultimately achieved in 1986.[120] Schrock and coworkers knew an alkylidene on a highly oxidized metal center, with a low coordination number, had to be synthesized.

The first d^0 complex prepared by Schrock was Ta(CH-t-Bu)(CH-t-Bu)$_3$,[121] but this highly oxidized catalyst showed no productive metathesis. The next catalyst Schrock synthesized was W(O)(CH-t-Bu)$(PMe_3)_2Cl_2$, which showed metathesis activity in the presence of a Lewis acid.[122] It was thirteen years later before the first metathesis active four coordinate, d^0, tungsten alkylidene was developed (Figure 1.22).[123]

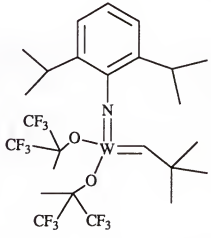


Figure 1.22. Schrock's Lewis acid free alkylidene.

The other three coordination sites were occupied by one imido and two alkoxide ligands chosen for their steric and electronic nature respectively. The aromatic imido ligand was chosen to inhibit deactivating dimerization reactions which can occur if the four coordinate tungsten alkylidene does not have enough stabilizing steric bulk.[124] Moreover, the electronic nature of the alkoxide ligand effects the electrophilicity of the metal center thereby changing the reactivity of the catalyst. For instance, when t-butoxide ligand is employed, cis-2-pentene is metathesized at a rate of only 2 turnovers/h while under

identical conditions, the more electron withdrawing hexaflouro-t-butoxide metathesized cis-pentene at the rate of 1000 turnovers/min.[125] Experimental evidence has shown that the increased electrophilicity of the metal center stabilizes the metallocyclobutane, allowing productive metathesis to occur. However, if a more electron withdrawing alkoxide ligand ($O(CF_3)_2CF_2CF_2CF_3$) is used, the metallocyclobutane is stabilized to the extent that it becomes unreactive.[124,126]

The size of the alkylidene also had to be considered in the reactivity of the catalyst. As the alkylidene ligand's steric bulk is increased there is also an increase in catalyst stabilization which translates to a decrease in reactivity. For example, the neopentylidene ligand is 100 times less reactive than the propylidene analog, but due to its increased stabilization the neopentylidene is a more effective ligand.[124] This development which began in 1973 concluded with the synthesis of a well defined alkylidene whose reactivity and stability was unsurpassed at that time. It was not until the evolution of the molybdenum analog that the true scope of Schrock's alkylidenes was understood.[127]

It was discovered that the molybdenum alkylidene is less polarized and more tolerant to functionality. For example, the molybdenum catalyst was tolerant to carbonyls, ethers, and amides, enabling the use of these functionalities in the synthesis of polymers and heterocycles.[128-32] The catalyst is limited still by the requirement that oxygen, acids, alcohols, and nucleophiles, be excluded, which was also true with the tungsten catalyst.

The discovery of the Lewis acid free alkylidene opened new avenues in the polymerization of olefins, even though many important discoveries had already been developed in the commercialization of high molecular weight unsaturated polymers. For example, the ring-opening metathesis polymerization of strained cyclic olefins, polymerized with Lewis acid classical

catalyst systems, became a very important route in polymerizing industrially useful materials. Three polymers have had commercial success, *trans*-poly(norbornene),[133] *trans*-poly(octenamer),[134] and poly(dicyclopentadiene).[135] These polymers are also known by their trade mark names Norosex™, Vestenamer™, and Metton™ respectively.

Ring-opening polymerizations are typically enthalpically driven due to the release of ring strain in 3 and 4-membered rings and non-bonded strain for 8,9 and 10-membered rings resulting from intra-ring interactions. However, rings with 5, 6, and 7-members are largely dependent on the reaction conditions since the entropy and enthalpy terms are similar.[136]

Lewis acid free catalysts have increased the control of ring-opening metathesis polymerization whereby the propagating carbene is living. This provides a route to the formation of block copolymers.[137-140] Controlling propagation generates polymers with narrow molecular weight distributions and desired degrees of polymerization, depending on the ratio of monomer to initiator concentrations.

The early developments of living metathesis polymerizations employed a highly strained titanacyclobutane containing a fused cyclopropane unit.[141] The release of ring strain in the initiation step promoted productive metathesis with this active catalyst. With the onset of Schrock's alkylidene, it became easier to control the reactivity toward strained olefins, in comparison to the linear olefins in the polymer backbone. This leads to less chain transfer and lower polydispersities.[124,142]

In the early 1990's, Schrock's alkylidenes were thought to be the quintessential catalyst system because of the control of propagation. There still exists problems with the catalyst system which limits its utility, for example, air stability, thermal stability, and its intolerance to protic media. It was not until

recently that Grubbs *et al.*[143] discovered a ruthenium based catalyst which enables the polymerizations of oxonorbornene in aqueous systems. This unprecedented discovery was followed by the synthesis of a preformed ruthenium carbene which is tolerant to alcohol functionality, air stable, and tolerant to protic media.[144,145] Grubbs' catalyst system appears to be much more tolerant to functionality in comparison to Schrock's molybdenum alkylidene and also capable of producing living polymers.

Recently, Grubbs has employed a Lewis acid free alkylidene in the synthesis of telechelic polybutadienes.[146] The generation of these telechelics is based on the premise that acyclic olefins act as chain transfer agents in ring-opening metathesis polymerizations, whereby the polymer's molecular weight is regulated. When α,ω-difunctional olefins are employed as chain transfer agents, difunctional telechelic polymers can be synthesized. A protected allylic diol was used as the chain transfer agent in the polymerization of cyclooctadiene, and resulted in the preparation of telechelic polybutadiene. As shown in Figure 1.23, the protecting groups were removed and α,ω-hydroxypolybutadiene was formed where the functionality was calculated to be 1.7-1.9.[146] When an additional methylene spacer was added between the olefin and the silyl ether (1,6-bis(*t*-butyldimethylsiloxy)-3-hexene), near quantitative yields of telechelic polymer were obtained. It was thought that the β-oxygen was providing a competitive decomposition pathway for the alkylidene, thereby hindering the quantitative conversion to telechelic.

Grubbs has briefly mentioned the employment of the preformed ruthenium alkylidene in the synthesis of α,ω-hydroxypolybutadiene. Due to the functional tolerance of this catalyst, the diol chain transfer agent is not protected. When chain transfer agent 1,6-hydroxy-3-hexene is used, preliminary results

show that there is close to quantitative conversion to telechelic, however, the allylic diol still creates telechelics with a functionality less than 2.0.[147]

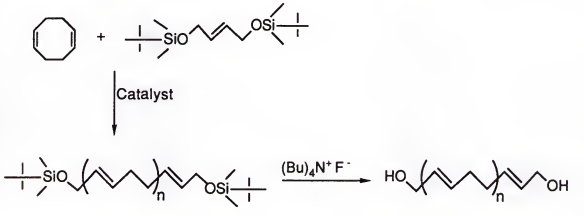


Figure 1.23. Synthesis of α,ω-hydroxypolybutadiene with a well defined catalyst system.

Acyclic Diene Metathesis

Acyclic diene metathesis (ADMET) is a step polymerization, condensation type reaction wherein an equilibrium is established between monomer and products (polymer and a small molecule). The equilibrium can be shifted toward polymer if the small condensed molecule is removed (Figure 1.24). The propagation in ADMET polymerization proceeds through a step growth process whereby monomer is consumed early in the reaction to form dimers, trimers, tetramers etc.



Figure 1.24. Acyclic diene metathesis (ADMET) polymerization.

This step polymerization technique is best described by the Carothers[148] equation:

$$Xn = 1 / (1-p)$$

where Xn is the degree of polymerization, and p is the extent of reaction. A plot of this equation reveals the need for high conversion (> 99%) before high molecular weight polymer is produced (Figure 1.25).

A requirement for high conversion is perfect stoichiometric balance of functional groups in the reaction. If stoichiometric imbalance occurs the degree of polymerization will decrease as shown in the following equation:

$$Xn = 1 + r / (1 + r - 2rp)$$

where r ($r < 1$) is the stoichiometric imbalance ratio and Xn and p have already been defined in Carothers equation.

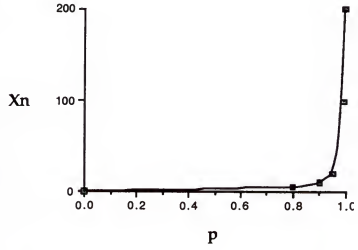


Figure 1.25. Plot of the Carothers equation.

Classical catalyst systems have been used in the attempt to produce high polymer from α,ω-dienes, and as Dall'Asta *et al.*[149] found when 1,5-hexadiene was catalyzed by $WCl_6/Et_3Al_2Cl_3/MeCCl(OH)CH_2Cl/-PPh_3$, the result was a linear oligomer with a degree of polymerization up to 8. Similar results were also found by Doyle[150] and Zuech[151] *et al.* where the classical catalyst system did not generate high polymer due to side reactions caused by the ill-defined catalyst system.

The absence of Lewis acidity appears to be important in avoiding cationic, vinyl addition. Wagener *et al.*[152] demonstrated that with a classical catalyst system the attempted metathesis of styrene led predominantly to the vinyl addition product, polystyrene. With this data it became apparent that a Lewis acid free catalyst must be used to produce polymer from α,ω-dienes. The same metathesis reaction of styrene was attempted with a Lewis acid free catalyst, Schrock's tungsten alkylidene, and *trans*-stilbene was metathetically generated in quantitative yield.[153]

With this new information at hand, the first ADMET polymerization was successfully demonstrated by condensing 1,9-decadiene to polyoctenamer.[153] The ADMET polymerization mechanism is shown in Figure 1.26. It is generally agreed that the mechanism begins with π-coordination of the nucleophilic olefin to the electrophilic metal. As shown in the mechanism scheme, the olefin metal complex forms a metallocyclobutane and productively cleaves yielding a new substituted alkylidene. The substituted alkylidene exchanges with monomer to form dimer and the methylidene. The methylidene then metathesizes with monomer resulting in the evolution of ethylene and the regeneration of the substituted alkylidene. This catalytic cycle continues until all monomer is consumed or when the polymer precipitates from solution.

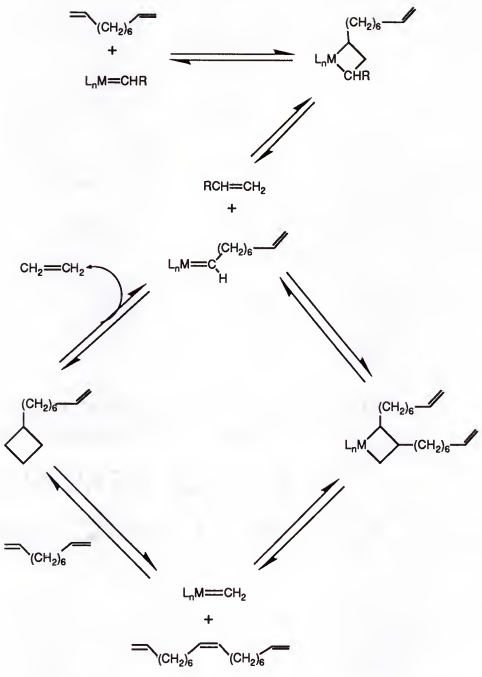


Figure 1.26. Acyclic diene metathesis polymerization mechanism.

This step condensation equilibrium polymerization has provided a novel synthetic approach in producing unsaturated polymers such as hydrocarbon polymers and copolymers,[153-155] polyferrocenes,[156] polyketones,[157]

polycarbonates,[157] polyethers,[159] polyesters,[160] polysiloxanes,[161] polysilanes,[162] and polysulfides.[163] The polymerization of functionalized monomers has given a better understanding of the interaction between the alkylidene and the corresponding functionality. For instance, when a carbonyl functional group is present, two methylenes are required to separate the alkylidene from the carbonyl or a negative neighboring group effect exists. This negative neighboring group effect is thought to be caused by either the coordination of the carbonyl to the metal center, or by polarization of the alkylidene by the electron withdrawing carbonyl (Figure 1.27).[160] This process competes with productive metathesis, either decreasing the rate of reaction or completely inhibiting the reaction. Carbonyls are not the only functionality which exhibit the negative neighboring group effect; similar interactions occur when an allylic ether is employed.[146]

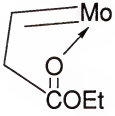


Figure 1.27. Negative neighboring group effect of an allylic ethyl ester.

Since ADMET is step condensation, equilibrium chemistry, the opportunity exists to reverse the reaction from polymer to monomer depending on reaction conditions (Figure 1.28). ADMET chemistry is void of any competing or side reactions. It enjoys the clean reversibility which enables the depolymerization chemistry to synthesize well defined macromolecules. This is in contrast to degradation chemistry which utilizes classical catalyst systems,

and results in the loss of unsaturation, ill-defined end groups, and cationic side reactions.

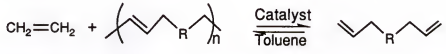


Figure 1.28. Acyclic diene metathesis depolymerization chemistry.

Acyclic diene metathesis depolymerization was demonstrated with polyoctenamer under a positive pressure of ethylene using Schrock's tungsten alkylidene catalyst[123] $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)W{=}CH(CH_3)_2Ph$.[164] The products were vinyl terminated oligomers exhibiting a number average molecular weight of about 1000, according to gel permeation chromatography (polystyrene standards). Other unsaturated polymers (polybutadiene, polyisoprene, and poly[styrene-*b*-butadiene] also were depolymerized to oligomers using identical conditions, producing number average molecular weights also in the range of 1000.[165]

This process of cross metathesizing olefins with ethylene was first reported by Bradshaw *et al.* [166] in which he termed the process ethenolysis. The utility of ethenolysis has had vast applications in degradation of polymers and the synthesis of compounds with terminal olefins. For example, long chain unsaturated fatty acid triglycerides have been cometathesized with ethylene to produce lower molecular weight fatty oils through this non-destructive pathway (Figure 1.29).[167]

While polybutadiene could be depolymerized to medium sized oligomers, numerous attempts to synthesize telechelics with a number average molecular weight less than 1000 were unsuccessful. Apparently the catalyst

decomposes over a period of time in the presence of ethylene, inhibiting quantitative depolymerization.

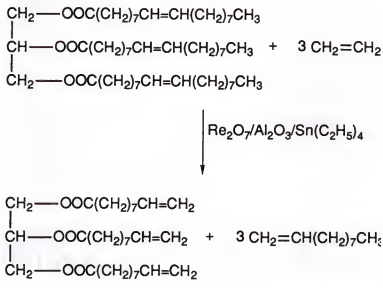


Figure 1.29. Ethenolysis of trioleylglycerol.

In this dissertation, substituted depolymerizing agents are employed in the quantitative depolymerization of 1,4-polybutadiene. A structure/property relationship between the catalyst and the functionalized olefin has been probed in an effort to synthesize a variety of α,ω-substituted telechelics. Through this exploration the depolymerization mechanism has been elucidated, which has allowed for the development of a new depolymerization reaction scheme.

CHAPTER 2

EXPERIMENTAL

Instrumentation and Analysis

^{1}H and ^{13}C NMR spectra were obtained with a Varian XL-200 (200 MHz) or a GE QE-300 (300 MHz) Series NMR Superconducting Spectrometer systems. Chloroform-*d* ($CDCl_3$) or benzene-d_6 were used as solvents and all chemical shifts reported are internally referenced to tetramethylsilane (TMS), $CDCl_3$, or benzene. Quantitative ^{13}C NMR spectra were run for 8-10 h with a pulse delay of 15 s, and number average molecular weight (M_n) were determined by integrating internal olefin carbon resonances vs. endgroup carbon resonances. Infrared data were recorded on a Perkin-Elmer 281 infrared spectrometer or a BioRad FTS/40A infrared spectrometer. Analyses were performed between NaCl plates for neat liquids or KBr pellets for solids.

Gel permeation chromatography (GPC) analysis were obtained using a Waters Associates 6000A liquid chromatography delivery system equipped with a U6k injector and a differential refractometer detector. Two Phenomenex 7.8 mm x 30 cm cross linked polystyrene gel columns were coupled consecutively, a 500-Å followed by a 1000-Å. When high molecular weight polymers were analyzed by GPC, 10^4Å and 10^5Å columns were coupled. The eluting solvent was HPLC grade tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Filtered (50 um) polymer samples were dissolved in THF (0.2-0.5 % w/v) and injected (10-40 uL). Retention times were calibrated against polybutadiene standards

(Polysciences, Inc.) ranging from M_w = 233000, 183000, 24000, 2760, 982, and 439 where $M_w/M_n \leq 1.07$.

Mass spectroscopy data were obtained with a Finnigan 4500 Gas Chromatograph / Mass Spectrometer (GC/MS) using chemical ionization (CI) or electron ionization (EI) techniques as indicated.

Elemental analyses were performed by Atlantic Microlab, Inc.

Materials and Techniques

The Lewis acid free catalysts used in the depolymerizations, $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)M{=}CHC(CH_3)_2Ph$, where M = W [125] and Mo [127], will be designated as catalyst 1 and 2 respectively. Toluene was extracted with cold concentration sulfuric acid followed by basic potassium permanganate and distilled from potassium benzophenone ketyl into a receiving flask which contained a sodium/potassium (NaK) alloy. Methylene Chloride was distilled and dried over potassium oxide (P_2O_5). The solvents were degassed by several freeze-thaw cycles. 1,4-Polybutadiene was obtained from the DeSimone group at the University of North Carolina at Chapel Hill and Aldrich. The DeSimone group anionically polymerized 1,4-polybutadiene (2) (M_n = 87,000), with a microstructure of 94% 1,4 content and polydispersity of 1.04. 1,4-Polybutadiene (15) purchased from Aldrich was 98 % cis and had a $M_n \geq$ 233,000 , which was higher than our GPC columns and standards could accurately measure. NATSYN 2200, 1,4-polyisoprene containing an antioxidant, was obtained from Goodyear Tire and Rubber Company where the $M_n \geq$ 233,000. Butyl 365, [poly(isoprene-*b*-butylene)] , was obtained from Exxon Chemical Corporation where the $M_n \geq$ 233,000. A silicone oil diffusion

pump coupled with a mechanical pump high vacuum manifold system (10^{-6} mmHg) was used for polymer degassing and monoene manipulations.

Polymer was twice dissolved in toluene or methylene chloride and precipitated in methanol before it was degassed. The polymer was placed in a reaction flasks equipped with Kontes™ high vacuum valves and dissolved in dried toluene or methylene chloride. By means of removing solvent *in vacuo*, the polymer was degassed.

All depolymerizing agents, except allylchlorodimethylsilane, allylphthalimide, and N,N-(*tert*-butoxycarbonyl)allylamine; were dried over calcium hydride and degassed by several freeze-thaw cycles, then vacuum transferred into an evacuated reaction flask, containing degassed polymer and a magnetic stir bar. Before catalyst was added, a GC of the monoene was taken to insure at least 99.95 % purity. Allylchlorodimethylsilane (Aldrich) was purified as stated above, with the exception of calcium hydride. Allylphthalimide and N,N-(*tert*-butoxycarbonyl)allylamine were first recrystallized from methanol and then sublimed.

Catalyst was added in the glove box under argon, where the repeat unit of polymer to catalyst ratio was 1000:1. When applicable, ethylene was removed *in vacuo*. Dry toluene was vacuum transferred into the reaction flask and the reaction was allowed to stir for 48 h.

When ethylene was employed as the depolymerizing agent; catalyst, polymer, and toluene were added analogous to what was stated above. Ethylene, from a Matheson gas cylinder (99.9%), was introduced into the reaction flask through a port in the manifold of the vacuum line. A positive pressure of 2.0 atm. was maintained throughout the reaction.

Reactions were terminated with exposure to oxygen or the atmosphere, depending if the depolymerizing agent was hydrolyzable. Volatiles were

removed *in vacuo* and analyzed. Non-volatile oligomers were dissolved in toluene, passed through an alumina column, and analyzed.

Synthesis and Characterization

Depolymerization of 1,4-Polybutadiene with Ethylene (1). Degassed 1,4-polybutadiene (2) (0.65 g, 12 mmol of repeat units) was placed in a reaction flask with catalyst 1 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)W=CHC$(CH_3)_2$Ph, (50 mg, 6.03 x 10^{-2} mmol) and dry toluene. Ethylene, C. P. (99.9%) was obtained from Matheson Gas Products, Inc. and used without further purification. Excess ethylene was added into the reaction flask at a pressure of 2.0 atm. Depolymerization was carried out at room temperature for 48 h, after which the volatiles were vacuum transferred and characterized. Oligomers remained in the reaction flask and were characterized. Volatile characterization: GC/MS(EI): M^+ = 82; M(100) = 67 (1,5-hexadiene); Oligomer characterization: ^{1}H NMR ($CDCl_3$) δ 2.05(br,4H), 5.40(br,2H), 5.65(br,2H). ^{13}C NMR ($CDCl_3$) δ 27.25, 129.41, 130.12. GPC (THF) M_n = 1700, PDI = 3.09.

Attempted Bulk Depolymerization of 1,4-Polybutadiene with Ethylene (3). 1,4-Polybutadiene (2) (1.01 g, 9.25 mmol of repeat units) and catalyst 1 (100 mg, .12 mmol) were reacted as stated in 1, except there was no toluene added to the reaction. The catalyst was absorbed into the polymer but no apparent reaction occurred.

Synthesis of Bis(trimethylsilyl)-2-butene (4). Degassed allyltrimethylsilane (Aldrich) (5) (1 mL) was added to catalyst 1 (5 mg) in 25 mL round bottom equipped with a stir bar. The reaction was carried out in the glove box for 1 h

and ethylene evolved as bis(trimethylsilyl)-2-butene was produced. The reaction was quantitative and characterized. ^1H NMR ($CDCl_3$) δ 0.00(s,18H), 1.50(d,4H), 5.40(t,2H). ^{13}C NMR ($CDCl_3$) δ 0.00, 23.50, 123.25. Anal. Calc. (found): C, 59.93 (60.04); H, 12.04 (12.08).

Depolymerization of 1,4-Polybutadiene with Allyltrimethylsilane with Catalyst 1 (6). Degassed 1,4-polybutadiene (2) (1.0 g, 18.5 mmol of repeat units) was added to catalyst 1 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)$-$W{=}CHC(CH_3)_2Ph$ (20 mg, 2.41 x 10^{-3} mmol). Allyltrimethylsilane (Aldrich) (5) (25 mL, .173 mol) was vacuum transferred into a reaction flask equipped with a magnetic stir bar. Ethylene evolved and was removed *in vacuo*. Toluene (25 mL) was vacuum transferred into the reaction and the solution was allowed to stir for 48 h. The reaction was terminated by exposure to air and the volatiles were removed *in vacuo*. The non-volatile oligomers were dissolved in toluene passed through an alumina column (100%). ^1H NMR ($CDCl_3$) δ 0.00(br), 1.50(br), 2.05(br), 5.40(br). ^{13}C NMR ($CDCl_3$) δ 0.00, 21.43, 35.72, 123.25. GC/MS: M^+ = 308, 362, 416; M(100) = 127. GPC (THF) M_n = 318, PDI = 1.20. IR spectrum: ν 1725 (C=C), 1250 (Si-C). Anal. Calc. (found): C, 74.68 (74.14); H, 11.63 (11.38).

Depolymerization of 1,4-Polybutadiene with Allyltrimethylsilane with Catalyst 2 (7). Degassed 1,4-polybutadiene (2) (1.0 g, 18.5 mmol of repeat units) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)$-$Mo{=}CHC(CH_3)_2Ph$ (20 mg, 2.41 x 10^{-3} mmol). Allyltrimethylsilane (Aldrich) (5) (25 mL, .173 mol) was vacuum transferred into a reaction flask equipped with a magnetic stir bar. The reaction proceeded analogous to 6 (100%). ^1H NMR ($CDCl_3$) δ 0.00(br), 1.50(br), 2.05(br), 5.40(br). ^{13}C NMR ($CDCl_3$) δ 0.00, 21.43,

35.72, 123.25. GC/MS: M^+ = 308, 362; M(100) = 127. GPC (THF) M_n = 325, PDI = 1.07. IR spectrum: v 1725 (C=C), 1250 (Si-C).

Synthesis of Bis(chlorodimethylsilyl)-2-butene (8). Allylchlorodimethylsilane (Aldrich) (2 mL, 1023 eq) was degassed and vacuum transferred into a dry reaction flask equipped with a stir bar. Catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (1 eq) was added to the flask and ethylene evolved. After 12 h the reaction proceeded quantitatively. ^{1}H NMR ($CDCl_3$) δ 0.43(s,12H), 1.75 (m,4H), 5.34 (m,2H). ^{13}C NMR ($CDCl_3$) δ 1.20, 24.88, 122.68, 123.98. HRMS (EI): M/Z, 241.0296, Calc. 240.0324.

Depolymerization of 1,4-Polybutadiene with Allylchlorodimethylsilane (9). Degassed 1,4-polybutadiene (2) (.65 g, 12 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol). Allylchlorodimethylsilane (Aldrich) (10 g, 74 mmol) was vacuum transferred into the reaction flask equipped with a stir bar, and the reaction proceeded analogous to the synthesis of 7 (100%). ^{1}H NMR ($CDCl_3$) δ 0.45(s,12H), 1.68(trans) (d,4H), 1.75(cis)(d,4H), 2.05(m,4H), 5.34(m,4H). ^{13}C NMR ($CDCl_3$) δ 1.11, 24.63, 32.96, 129.50 (cis), 130.92 (trans). GC/MS: M^{+1} = 295, M(100) = 259. GPC (THF) M_n = 426, PDI = 1.04. IR spectrum: v 1735 (C=C), 1250 (Si-C).

Synthesis of Ethyl 4-Pentenoate (10). 4-Pentenoic acid (10 mL, 97 mmol), ethanol (5.8 mL, 97 mmol), and a catalytic amount of conc. H_2SO_4, were placed in a 50 mL round bottom flask containing a stir bar. A reflux condenser was placed on the flask and the reaction refluxed for 3 h. The product was washed with sodium bicarbonate (3 x 10 mL) and water (3 x 10 mL). Compound

10 was dried with magnesium sulfate and distilled (bp = 142-146°C) (92 %). ^{1}H NMR ($CDCl_3$) δ 1.27(t,3H), 2.35(t,2H), 2.37(m,2H), 4.13(q,2H), 5.00(t,2H), 5.75(m,1H). ^{13}C NMR ($CDCl_3$) δ 14.17, 28.85, 35.55, 60.22, 115.34, 136.68, 172.94. Anal. Calc. (found): C, 65.61 (65.78); H, 9.43 (9.47).

Synthesis of Bis(carboethoxy)-3-hexene (11). Ethyl 4-pentenoate (10) (1 mL) and catalyst 2 [$(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol) were reacted in an analogous procedure for the synthesis of 4. Upon addition of catalyst 2, ethylene evolved. After 12 h., there was 55% conversion to 11. Next, 5 mg of catalyst 2 was added and allowed to react for 3 hours. The reaction was quantitative. ^{1}H NMR ($CDCl_3$) δ 1.27(t,3H), 2.35(t,2H), 2.37(m,2H), 4.13(q,2H), 5.42(m,2H)(cis), 5.35(m,2H)(trans). ^{13}C NMR ($CDCl_3$) δ 14.17, 28.85, 35.55, 60.22, 128.95(cis), 129.36(trans), 172.94. Anal. Calc. (found): C, 63.18 (63.25); H, 8.78 (8.79).

Depolymerization of 1,4-Polybutadiene with Bis(carboethoxy)-3-hexene (12). Degassed polybutadiene (15) (Aldrich) (0.55 g, 10 mmol) was added to catalyst 2 [$(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol). Compound 11 (5.0 g, 42 mmol) was vacuum transferred into the reaction flask. Toluene (25 mL) was dried over sodium potassium alloy and added. The reaction was allowed to stir for 12 h. Volatiles were removed *in vacuo* and oligomers were purified by an alumina column (100%). ^{1}H NMR ($CDCl_3$) δ 1.27(t,3H), 2.05(m,4H), 2.35(t,2H), 2.37(m,2H), 4.13(q,2H), 5.40(m,4H). ^{13}C NMR ($CDCl_3$) δ 14.17, 27.85, 34.55, 60.22, 128.95(cis), 129.36(trans), 172.94. GC/MS: M^{+1} = 283, 337 M(100) = 237,337. GPC (THF) M_n = 295, PDI = 1.07. IR spectrum: ν 1725(C=O), 1640(C=C), 1240 (C-O).

Synthesis of Bis(acetoxy)-2-octene (13). 4-Penten-1-yl acetate (Aldrich) (1 mL) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (25 mg, 3.01 x 10^{-2} mmol) were added to a reaction flask in the glove box. The reaction was analogous to the procedure in the synthesis of 4. Upon addition of catalyst, ethylene evolved and the reaction was quantitative. ^{1}H NMR ($CDCl_3$) δ 1.74(m,4H), 2.02(s,6H), 2.04(m,4H), 4.09(t,4H), 5.45(m,2H). ^{13}C NMR ($CDCl_3$) δ 20.84, 23.45, 28.29(cis), 28.72(trans), 63.70, 129.29(cis), 129.77(trans), 170.98. Anal. Calc. (found): C, 63.18 (63.20); H, 8.78 (8.79)

Depolymerization of 1,4-Polybutadiene with Bis(acetoxy)-2-octene (14). Degassed 1,4-polybutadiene (2) (.50 g, 9 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol) and bis(acetoxy)-2-octene (13) (5.0 g, 42 mmol) was vacuum transferred into the reaction flask. The reaction proceeded analogous to the synthesis of 7 (100%). ^{1}H NMR ($CDCl_3$) δ 1.74(m,4H), 2.05(14H,m), 4.09(t,4H), 5.45(m,4H). ^{13}C NMR ($CDCl_3$) δ 20.84, 23.45, 28.29, 28.72, 32.55, 63.70, 129.29, 130.77, 170.98. GC/MS: M^{+1} = 283, M(100) = 163. IR spectrum: ν 1740(C=O), 1650-(C=C), 1240 (C-O).

Synthesis of *t*-Butyldimethylsilyl Butene Ether (16). *t*-Butyldimethylsilyl chloride (11.8 g, 80 mmol) and imidazole (12.2 g, 180 mmol) were added to a 150 mL Schlenck tube equipped with a stir bar and a Suba™ septum. The reaction flask was cooled to 0°C and 4-buten-1-ol (5.0 g, 73 mmol) was added via a syringe. The reaction was allowed to warm to rt and stir for 1h. The product was extracted with ether, washed with water (3 x 15 mL), dried with magnesium sulfate, and the ether was removed via rotoevaporation. Compound 16 was fractionally distilled (bp = 126-128°C)(88%). ^{1}H NMR

($CDCl_3$) δ 0.05(s,6H), 0.90(s,9H), 2.25(m,2H), 3.60(t,2H), 5.10(dd,2H), 5.75(m,1H). ^{13}C NMR ($CDCl_3$) δ 0.50, 18.17, 26.15, 31.75, 36.43, 63.85, 117.54, 135.27. IR spectrum: ν 1640 (C=C), 1251 (Si-Me), 1081 (C-O), 875 (Si-O). Anal. Calc. (found): C, 65.15 (65.26); H, 10.93 (10.95).

Depolymerization of 1,4-Polybutadiene with *t*-Butyldimethylsilyl Butene Ether (17). Degassed polybutadiene (15) (0.50 g, 9 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.03 x 10^{-3} mmol) and *t*-butyldimethylsiloxy butene ether (16) (5.0 g, 29.5 mmol). The reaction proceeded analogous to the synthesis of 7 (100%). ^1H NMR ($CDCl_3$) δ 0.05(s,12H), 0.90(s,18H), 2.05(m,4H), 2.25(m,4H), 3.60(t,4H), 5.45(m,2H). ^{13}C NMR ($CDCl_3$) δ 0.50, 20.10, 27.75, 34.18, 38.00, 63.85, 129.54, 130.27, 132.10, 134.05. GPC (THF) M_n = 362, PDI = 1.23. GC/MS: M^{+1} = 399, 453 M(100) = 135, 189.

Synthesis of Bis(*t*-butyldimethylsiloxy)-2-butene (18). *t*-Butyldimethylsilyl chloride (23.6 g, 160 mmol) and imidazole (12.2 g, 180 mmol) were added to a 150 mL Schlenck tube equipped with a stir bar and a Suba™ septum. The reaction flask was cooled to 0°C and 2-butene-1,4-diol (6.6 g, 75 mmol) was added via a syringe. The reaction proceeded analogous to the synthesis of 16. Compound 18 was fractionally distilled (bp = 135-137°C @ 1 mmHg) (77 %). ^1H NMR ($CDCl_3$) δ 0.05(s,12H), 0.95(s,18H), 4.25(d,4H), 5.50(m,2H). ^{13}C NMR ($CDCl_3$) δ 0.50, 18.95, 26.00, 59.95, 130.14. IR spectrum: ν 1640 (C=C), 1251 (Si-Me), 1081 (C-O), 875 (Si-O). Anal. Calc. (found): C, 60.72 (61.10); H, 11.45 (11.52).

Depolymerization of 1,4-Polybutadiene with Bis(*t*-butyldimethylsiloxy)-2-butene (19) Degassed polybutadiene (15) (0.50 g, 9 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-Mo=CH$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol) and bis(*t*-butyldimethylsiloxy)-3-butene (5.0 g, 12.5 mmol). The reaction proceeded analogous to the synthesis of 7 (88%). ^{1}H NMR ($CDCl_3$) δ 0.05(s,12H), 0.90(s,18H), 2.05(m,4H), 4.05(d,4H)trans, 4.07(d,4H)cis, 5.72(m,2H). ^{13}C NMR ($CDCl_3$) δ 0.50, 19.10, 26.75, 32.18, 32.56, 63.85, 64.04, 129.64, 130.17. GPC (THF) M_n = 397, PDI = 1.05. GC/MS: M^{+1} = 371, 425 M(100) = 107, 161.

Synthesis of Macrocyclic Butadiene (20). Degassed polybutadiene (2) (0.65 g, 12 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-Mo=CH$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3}) were placed in a reaction flask equipped with a stir bar. Toluene (25 mL) was vacuum transferred to the reaction flask, and the reaction was allowed to stir for 48 h. The reaction was exposed to the atmosphere, and the volatiles were removed *in vacuo* (100%). ^{1}H NMR ($CDCl_3$) δ 2.05(m,4H), 5.35(m,2H). ^{13}C NMR ($CDCl_3$) δ 26.84, 33.47, 129.84, 130.05. GPC (THF) M_n = 185, PDI = 1.03. GC/MS: M^{+1} = 163, 217 M(100) = 121. Anal. Calc. (found): C, 88.83 (88.79); H, 11.17 (11.16).

Synthesis of N-(allyl)phthalimide (21). Allyl amine (4.1 g, 7 mmol) and toluene (150 mL) were placed in a 250 mL round bottom flask equipped with a Claisen adapter, dropping funnel, reflux condenser, and stir bar. The flask was cooled to 0°C and phthaloyl dichloride (14.5 g, 7 mmol) was added slowly. The reaction was warmed to rt and toluene was removed *in vacuo*. The resulting yellow solid was dissolved in THF, washed with 15% NaOH (aq.) (3 x 15 mL), and then water (3 x 15 mL). THF was removed *in vacuo*, and crude 21 was

recrystallized in a 90:10 methanol/water solution to yield a white solid (90%) (mp = 69-71°C). ^{1}H NMR ($CDCl_3$) δ 4.25(d,2H), 5.25(m,.2H), 5.90(m,1H), 7.65(dd,4H). ^{13}C NMR ($CDCl_3$) δ 40.01, 117.71, 123.27, 131.50, 132.08, 133.95, 167.88. Anal. Calc. (found): C, 70.58 (70.29); H, 4.84 (4.80); N, 7.48 (7.46).

Synthesis of Bis(phthalimido)-2-butene (22). N-(Allyl)-phthalimide (1 g, 5 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol) were added to a 50 mL round bottom flask equipped with a Kontes high vacuum valve and stir bar. The flask was placed on a high vacuum line under a dynamic vacuum, heated to 70°C, and stirred for 24 h. The crystals melted and ethylene evolved. After 24 h the liquid became a solid (mp = 212°C). ^{1}H NMR ($CDCl_3$) d 4.25(d,4H), 5.75(m,2H),, 7.70(dd,4H). ^{13}C NMR ($CDCl_3$) d 39.91, 123.51, 130.03, 132.06, 134.07.

Depolymerization of 1,4-Polybutadiene with Bis(phthalimido)-2-butene (23). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and bis(phthalimido)-2-butene (22) (5.0 g, 25 mmol). Methylene chloride (25 mL) was vacuum transferred from P_2O_5 and the reaction was stirred for 24 h. The volatiles were removed *in vacuo* and the oligomers were purified through an alumina column (100%). ^{1}H NMR ($CDCl_3$) δ 2.05(m), 4.25(d,4H)trans, 4.55(d,4H)cis, 5.70(m,4h). ^{13}C NMR ($CDCl_3$) δ 28.85, 39.35, 123.45, 127.78, 132.20, 134.05, 135.57, 168.13. GC/MS: M^{+1} = 401, 455, M(100) = 242, 160. GPC (THF) M_n = 345, PDI = 1.05.

Synthesis N-(*tert*-Butoxycarbonyl)allylamine (24). Allyl amine (6.5 g, 0.11 mol) and a 200 mL solution of 10% (w/v) of triethylamine in methanol were added to a 500 mL round bottom flask equipped with a condenser. Di-*t*-butyl dicarbonate was added, and the reaction was heated to 45°C for 10 minutes. Reaction was cooled and the solvent was removed *in vacuo*. The remaining yellow liquid was dissolved in ether, washed with satd. $NaHCO_3$ (3 x 15 mL), and then water (3 x 15 mL). The ether was dried over $MgSO_4$ and solvent removed via rotoevaporation to yield 24. Crude 24 was purified by distillation (bp = 80-83°C at .7 mmHg)(mp = 35°C)(73%). ^1H NMR ($CDCl_3$) δ 1.45(s,9H), 3.75(m,2H), 4.70(br,1H), 5.10(m,2H), 5.75(m,1H). ^{13}C NMR ($CDCl_3$) δ 28.31, 44.49, 79.24, 115.52, 134.91, 155.74. GC/MS: M^{+1} = 158, M(100) = 102. Anal. Calc. (found): C, 61.12 (61.14); H, 9.61 (9.64); N, 8.91 (8.90).

Synthesis of Bis(N-(*tert*-Butoxycarbonyl)amino)-2-butene (25). N-(*tert*-butoxycarbonyl)allylamine (24) (10 mg, 6.0 x 10^{-2} mmol) and catalyst 2 [$(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.03 x 10^{-3} mmol) were reacted in a NMR tube in deuterated toluene over an eight hour period (60%). ^1H NMR (C_6D_6) δ 1.40(s,18H), 3.65(m,4H), 4.70(s,2H), 5.60(m,2H).

Attempted Depolymerization of 1,4-Polybutadiene with N-(*tert*-butoxycarbonyl)allylamine (26). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 [$(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and N-(*tert*-butoxycarbonyl)-allylamine (24) (5.0 g, 25 mmol). Toluene (25 mL) was added and the reaction was stirred for 24 h. The reaction yielded starting material.

Attempted Depolymerization of 1,4-Polybutadiene with Diethyl Fumarate (27). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and diethyl fumarate (27). Toluene (25 mL) was added and the reaction was stirred for 24 h. The reaction yielded starting material.

Attempted Depolymerization of 1,4-Polybutadiene with Diethyl Maleate (28). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and diethyl maleate (Aldrich). Toluene (25 mL) was added and the reaction was stirred for 24 h. The reaction yielded starting material.

Attempted Cross Metathesis between 4,7-Dihydro-2-phenyl-1,3-dioxepin and 1,4-Polybutadiene (29). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and 4,7-dihydro-2-phenyl-1,3-dioxepin (Aldrich). Toluene (25 mL) was added and the reaction was stirred for 24 h. The reaction yielded starting material.

Attempted Cross Metathesis between 4,7-Dihydro-1,3-dioxepin and 1,4-Polybutadiene (30). Degassed polybutadiene (15) (0.50 g, 9.0 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and 4,7-dihydro-1,3-dioxepin (Aldrich). Toluene (25 mL) was added and the reaction was stirred for 24 h. The reaction yielded starting material.

Attempted Ring-Opening Polymerization of 4,7-Dihydro-2-phenyl-1,3-dioxepin (31). 4,7-Dihydro-2-phenyl-1,3-dioxepin (50 mg, 0.28 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.0 x 10^{-3} mmol) in the dry box, and was allowed to stir for 24 h. There was no apparent polymerization.

Attempted Ring-Opening Polymerization of 4,7-Dihydro-1,3-dioxepin (32). 4,7-Dihydro-1,3-dioxepin (Aldrich) (50 mg, 0.5 mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.0 x 10^{-3} mmol) in the dry box, and was allowed to stir for 24 h. There was no apparent polymerization.

Attempted Ring-Opening Polymerization of 4,7-Dihydro-2-phenyl-1,3-dioxepin in a NMR scale reaction (33). 4,7-Dihydro-2-phenyl-1,3-dioxepin (2 mg, 1.1 x10^{-2} mmol) (Aldrich) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)Mo{=}CHC(CH_3)_2Ph$ (30 mg, 3.6 x 10^{-2} mmol) in deuterated benzene. A ^1H NMR was taken over a 8 h time period and no apparent exchange occurred between the catalyst and 4,7-Dihydro-2-phenyl-1,3-dioxepin.

Attempted Ring-Opening Polymerization of 4,7-Dihydro-1,3-dioxepin in a NMR scale reaction (34). 4,7-Dihydro-1,3-dioxepin (Aldrich) (2 mg, 2.0 x 10^{-2} mmol) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)\text{-}Mo{=}CHC(CH_3)_2Ph$ (30 mg, 3.6 x 10^{-3} mmol) in deuterated benzene. A ^1H NMR was taken over a 8 h time period and no apparent exchange occurred between the catalyst and 4,7-Dihydro-1,3-dioxepin.

Attempted Synthesis of High Molecular Weight Polybutadiene Telechelics with Bis(*t*-butyldimethylsiloxy)-3-hexene (35). A 0.13 M solution of degassed 1,4-polybutadiene (0.50 g, 9 mmol) in dry toluene was placed in a 100 mL round bottom equipped with a stir bar and a Kontes™ high vacuum valve. Catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=$CHC(CH_3)_2Ph$ (5 mg, 6.0×10^{-3} mmol) and bis(*t*-butyldimethylsiloxy)-3-hexene (0.1 g, 0.3 mmol) were added to the solution in the glove box. After stirring for 48 h, the reaction was exposed to the atmosphere. Toluene was removed *in vacou* and the telechelics were analyzed. See text for analysis.

Depolymerization of 1,4-Polybutadiene with Bis(*t*-butyldimethylsiloxy)-3-hexene to form High Molecular Weight Telechelics (36). A 0.13 M solution of degassed 1,4-polybutadiene (0.50 g, 9 mmol) in dry toluene was placed in a 100 mL round bottom equipped with a stir bar and a Kontes™ high vacuum valve. Catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=$CHC(CH_3)_2Ph$ (5 mg, 6.0×10^{-3} mmol) was added and the reaction was stirred for 3 h. Bis(*t*-butyldimethylsiloxy)-3-hexene (0.1 g, 0.3 mmol) was added to the solution and toluene was immediately removed *in vacou*. The reaction was allowed to stir in the bulk for 24 h, and was then exposed to the atmosphere. The products were dissolved in toluene and precipitated in methanol (85%). ^1H NMR (C_6D_6) δ 0.00(s), 0.90(s), 2.05(br), 3.55(t), 5.45(br). ^{13}C NMR ($CDCl_3$) δ 0.30, 20.10, 27.75, 34.18, 38.00, 63.85, 129.54, 130.27, 132.10, 134.05. GPC (THF) M_n = 1100, PDI = 2.6.

Depolymerization of 1,4-Polybutadiene with Bis(*t*-butyldimethylsiloxy)-3-hexene to form High Molecular Weight Telechelics (37). Degassed 1,4-polybutadiene (0.50 g, 9 mmol) was placed in a 0.13 M solution of dry toluene

in a 100 mL round bottom equipped with a stir bar and a Kontes™ high vacuum valve. Catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (15 mg, 1.8 x 10^{-2} mmol) was added and the reaction was stirred for 3 h. Bis(*t*-butyldimethylsiloxy)-3-hexene (65 mg, 0.19 mmol) was added to the solution and toluene was immediately removed *in vacou*. The reaction proceeded analogous to 36 (100%). ^{1}H NMR ($CDCl_3$) δ 0.05(s), 0.90(s), 2.05(br), 3.60(t), 5.45(br). ^{13}C NMR ($CDCl_3$) δ 25.10, 27.75, 34.18, 38.00, 63.85, 129.54, 130.27, 130.50. GPC (THF) M_n = 2600, PDI = 1.75.

Depolymerization of Butyl Rubber with Bis(phthalimido)-2-butene (38). Degassed butyl rubber (0.50 g) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and bis(phthalimido)-2-butene (22) (5.0 g, 25 mmol). Methylene chloride (25 mL) was vacuum transferred from P_2O_5 and the reaction was stirred for 48 h. The volatiles were removed *in vacuo*. The resulting polymer was dissolved in methylene chloride and precipitated in methanol (100 %). GPC data showed an increase in the retention volume. The^1H NMR showed resonances typical for butyl rubber. IR spectrum: ν 1750(C=O), 1720-(C=O). Anal. found: C, 81.86; H, 12.76; N, 1.07.

Attempted Depolymerization of Butyl Rubber with Bis(*t*-butyldimethylsiloxy)-3-hexene (39). Degassed butyl rubber (0.50 g) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and bis(*t*-butyldimethylsiloxy)-3-hexene (5.0 g, 12.5 mmol). Toluene (25 mL) was vacuum transferred from sodium potassium alloy and the reaction was allowed to stir for 48 h. Additional catalyst 2 was added and the reaction was stirred for 48 h. The reaction yielded starting material.

Attempted Depolymerization of Polyisoprene with Bis(*t*-butyldimethylsiloxy)-3-hexene (40). Degassed polyisoprene (0.50 g) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (5 mg, 6.0 x 10^{-3} mmol) and bis(*t*-butyldimethylsiloxy)-3-hexene (5.0 g, 12.5 mmol). Toluene (25 mL) was vacuum transferred from sodium potassium alloy and the reaction was allowed to stir for 48 h. Additional catalyst 2 was added and the reaction was stirred for 48 h. The reaction yielded starting material.

Attempted Intramolecular Cyclization of Polyisoprene (41). Degassed polyisoprene (0.50 g) was added to catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph and toluene (25 mL) was vacuum transferred into the reaction flask from sodium potassium alloy. The reaction was allowed to stir for 48 h. Additional catalyst 2 was added and the reaction was stirred for 48 h. The reaction yielded starting material.(5 mg, 6.0 x 10^{-3} mmol) and toluene (25 mL) was vacuum transferred from sodium potassium alloy. The reaction was allowed to stir for 48 h. Additional catalyst 2 was added and the reaction was stirred for 48 h. The reaction yielded starting material.

^{1}H NMR Scale Reaction of the Attempted Intramolecular Cyclization of Polyisoprene (42). Degassed polyisoprene (5 mg, 7.0 x 10^{-2} mmol) was placed in an NMR tube along with catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=CHC$(CH_3)_2$Ph (15 mg, 1.8 x 10^{-2}) and deuterated benzene. The ^{1}H NMR was run over a 24 h period, and no apparent exchange occurred between the catalyst and polyisoprene.

Attempted Synthesis of Bis(cyano)-2-butene (43). Allylcyanide (Aldrich) (1 mL, 12 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-

$Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.03 x 10^{-3} mmol) were reacted in an analogous procedure for the synthesis of 4. After 12 h of stirring no apparent reaction occurred.

Synthesis of Pentenonitrile (44). Potassium cyanide (20 g, .15 mol) and ethylene glycol (100 mL) were placed in a 250 mL round bottom flask equipped with a thermometer, condenser, addition funnel, and stir bar. The reaction was heated to 100°C and 4-bromo-1-butene (9.77 g, .15 mol) was added slowly. The colorless solution became tan and was allowed to stir for 1h. Pentenonitrile was distilled from the reaction flask (bp = 146°C). ^1H NMR ($CDCl_3$) δ 3.15(,2H), 5.40(m,2H), 5.70(m,1H). ^{13}C NMR ($CDCl_3$) δ 21.39, 117.05, 119.63, 125.81. GC/MS(EI): M^+ = 81, M(100) = 41. IR spectrum: v 2240 (C≡N), 1640 (C=C).

Attempted Synthesis of Bis(cyano)-2-butene (45). Pentenonitrile (15) (1 g, 12 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)-$Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.03 x 10^{-3} mmol) were placed in a reaction flask in the glove box. After 12 h of stirring no apparent reaction occurred.

Attempted Synthesis of Bis(amino)-2-butene (46). Allyl amine (Aldrich) (1 mL, 13 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)$Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.03 x 10^{-3} mmol) were placed in a reaction flask in the glove box. After 12 h of stirring no apparent reaction occurred.

Attempted Synthesis of (47). Allyl alcohol (Aldrich) (1 mL, 13 mmol) and catalyst 2 $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)$Mo{=}CHC(CH_3)_2Ph$ (5 mg, 6.03 x

10^{-3} mmol) were reacted placed in a reaction flask in the glove box. After 12 h of stirring no apparent reaction occurred.

CHAPTER 3

SYNTHESIS OF PERFECTLY DIFUNCTIONAL α,ω-ALLYLSILANES

Ethylene Depolymerizing Agent

As described in chapter 1, the employment of a classical catalyst system in degradation chemistry causes side reactions thereby decreasing the functionality of the telechelic. Hence a more efficient route must be employed in the synthesis of difunctional telechelics via olefin metathesis degradation. The discovery of a Lewis acid free alkylidene led to the development of ADMET depolymerization chemistry whereby 1,4-polybutadiene is cleanly depolymerized to perfectly difunctional telechelics. Initially 1,4-polybutadiene was depolymerized under atmospheric pressure ethylene with Schrock's tungsten alkylidene, and the reaction yielded α,ω-vinyl-1,4-polybutadiene oligomers along with 1,5-hexadiene.[165] If the reaction had proceeded quantitatively, the monomeric unit 1,5-hexadiene would have been produced exclusively. Instead, the majority of the product mixture contained the divinyl terminated oligomers with a weight average molecular weight of 2000 according to gel permeation chromatography (GPC versus polybutadiene standards).[165] This chemistry was attempted to be optimized by increasing the ethylene pressure to 2.0 atm. The result was the formation of telechelics with a number average molecular weight of 1700 (1) (GPC versus polybutadiene standards) (Figure 3.1).

Schrock *et al.*[125] discovered that in the presence of 2.4 eq. of ethylene, the neopentyl tungsten alkylidene rapidly forms an isolable white crystalline metallocycle which has been analyzed by NMR spectroscopy. [168]

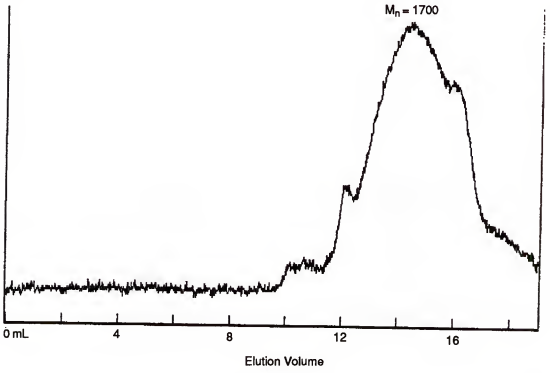


Figure 3.1. Gel permeation chromatograph of products formed (1) in the depolymerization of 1,4-polybutadiene (2) with ethylene.

A crystal structure of this compound was not published; however a similar metallocycle with analogous NMR resonances, $W(CH_2CH_2CH_2)(NAr)$-$[(OC(CF_3)_2(CF_2CF_2CF_3)]_2$, has been studied by x-ray crystollography (Figure 3.2).[125] The interesting characteristic of this crystal structure is the fact that the metallocycle is completely planar. This can be attributed to the lack of steric interactions between the metallacycle and the surrounding ligands. When steric interactions occur between substituents on the ring and/or with ligands in the coordination sphere, the result is the formation of a bent ring. It has been hypothesized that for an olefin to be exchanged the ring must be bent.[125]

These results have led to the employment of a functionalized olefin which would cause the deformation of the metallocycle thereby promoting quantitative depolymerization of 1,4-polybutadiene.

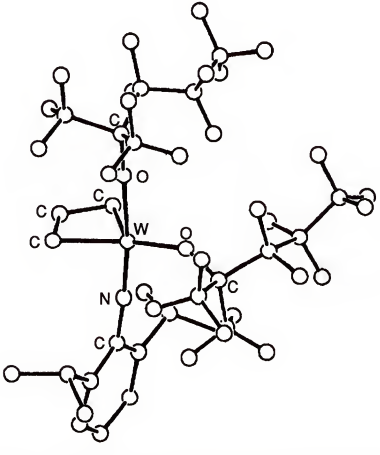


Figure 3.2. A crystal structure of $W(CH_2CH_2CH_2)(NAr)[(OC(CF_3)_2(CF_2C-F_2CF_3)]_2$.

The molybdenum alkylidene has never been employed in the presence of excess ethylene because the catalyst readily decomposes. Schrock has briefly alluded to the decomposition pathway whereby the highly oxidized, d^0 metal center of the metallocycle is reduced by either a β-hydride rearrangement or bimolecular coupling of methylene ligands.[128,168] The reaction mechanism illustrated in Figure 3.3 shows that propylene would be formed if a β-hydride rearrangement occurred, but there is no evidence of propylene formation.

However, NMR spectroscopy has identified the formation of the bimolecular coupling product, molydacyclopentane complex, which is proposed to decompose to give ethylene (Figure 3.3).

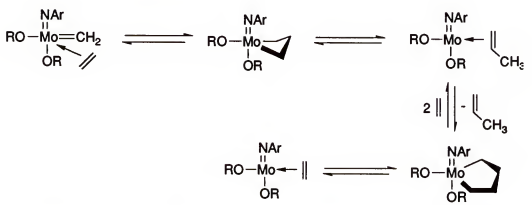


Figure 3.3. Proposed decomposition pathway of the molybdenum catalyst in the presence of excess ethylene.

Since Wagener and Smith[161,162] had previously established parameters in the metathesis of silicon acyclic dienes, it was understood that a methylene spacer must separate the olefin from the silicon functionality for productive metathesis to occur. Using this guideline, a variety of siloxane and carbosilane acyclic dienes were polymerized. For example, in Figure 3.4 diallyldimethylsilane was successfully polymerized with the neopentyl tungsten alkylidene.[161]

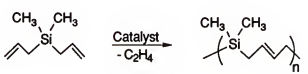


Figure 3.4. Acyclic diene metathesis polymerization of diallyldimethylsilane with catalyst $[CH_3(CF_3)_2CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)W=CHC$(CH_3)_2$Ph.

Schrock *et al.*[125] also showed in detail that vinyl silanes do not productively metathesize. For instance, vinyltrimethylsilane (vinylTMS) was reacted with the neopentyl tungsten alkylidene which afforded the non-catalytic products 3-methyl-3-phenyl-1-butene and the silated alkyidene (Figure 3.5). As shown in Figure 3.5, upon addition of excess vinylTMS, the isolable bis(trimethylsilyl)tungstacyclobutane was formed in equilibrium with the less favored silated alkylidene (K_{eq} = 1.4 x 10^{-3} M at 24°C in toluene). There was no evidence that the catalytic product bis(trimethylsilyl)ethene was synthesized.

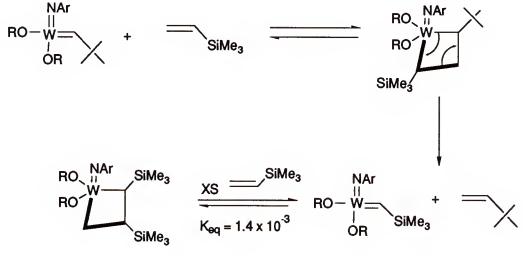


Figure 3.5. Metathesis of vinyltrimethylsilane.

Knowing the limitations of this chemistry allowed for the employment of a functionalized metathesis active depolymerizing agent, allyltrimethylsilane, in the depolymerization of 1,4-polybutadiene. The proposed mechanism in which this depolymerization proceeds is illustrated in Figure 3.6. Initially, the precatalyst (a) is metathesized with the monoene (b) to generate the symmetrical olefin (c) and a new alkylidene (d). The new alkylidene (d) and the polymer (e) form a trisubstituted metallacyclobutane which can productively

cleave affording an α-functionalized macromolecule (f) and the polymeric alkylidene (g). The alkylidene exchanges with the symmetrical olefin (c) and functionalizes the ω-position of the macromolecule (h). The catalytic cycle continues until every olefin is terminated by the depolymerizing agent.

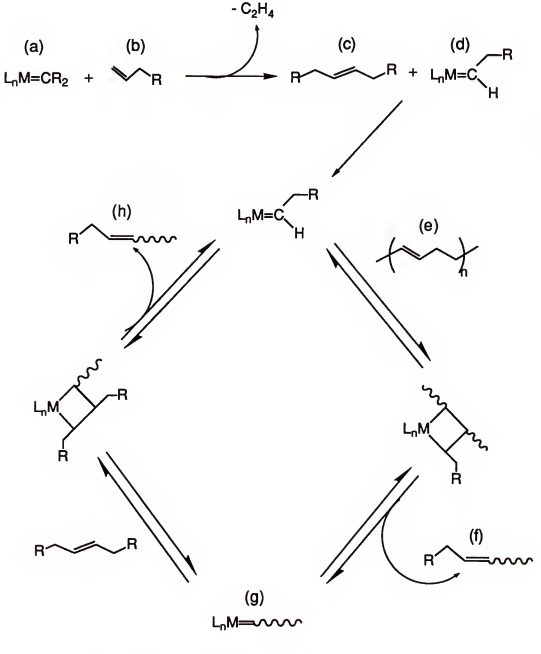


Figure 3.6. ADMET depolymerization cycle.

Allyltrimethylsilane Depolymerizing Agent with Tungsten Catalyst

The tungsten version of Schrock's alkylidene $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)W=$CH(CH_3)_2Ph$[125] (catalyst 1, Figure 3.7) was the first Lewis acid free catalyst used in ADMET depolymerization chemistry. Later, the molybdenum alkylidene $[(CF_3)_2CH_3CO]_2$(N-2,6-C_6H_3-*i*-Pr_2)Mo=$CH(CH_3)_2Ph$ (catalyst 2, Figure 3.7)[127] was utilitized more due to its tolerance to functionality. ADMET depolymerization chemistry began with the depolymerization of 1,4-polybutadiene (2) (M_n = 87000) (10 equiv/repeat units) with the *in situ* dimerized allyltrimethylsilane (4). Additional catalyst 1 was added (repeat unit/catalyst ratio 1000:1) along with toluene (50 mL) and the solution was allowed to stir for 48 h. The reaction was terminated by exposure to the atmosphere, and the volatiles, which were composed of toluene and allyltrimethylsilane dimer, were removed from the flask leaving behind perfectly difunctional α,ω-bis(trimethylsilyl)-1,4-polybutadiene (6) where n = 2, 3 and 4 (Figure 3.7).



R	Catalyst	n
-$CH_2Si(CH_3)_3$ (5)	1	2, 3, 4
-$CH_2Si(CH_3)_3$ (6)	2	1, 2
-$CH_2Si(CH_3)_2Cl$ (8)	2	1

Figure 3.7. Depolymerization of 1,4-polybutadiene with allylsilanes.

Evidence for perfect difunctionality is found in Figures 3.8, 3.9, and 3.10. Figure 3.8 shows the ^1H NMR spectra of allyltrimethylsilane and difunctional telechelic oligomers. These oligomers exhibited four resonances corresponding to the vinylic hydrogens (f) (5.35 ppm), the polybutadiene methylenes (e) (2.00 ppm), the allylic protons (c) (1.35 ppm), and the trimethylsilyl protons (d) (0.00 ppm). Incorporation of trimethylsilyl endgroups into the oligomers is demonstrated by the loss of its terminal vinylic proton (a) (6.00 ppm) and the appearance of allylic protons (c) (1.35 ppm).

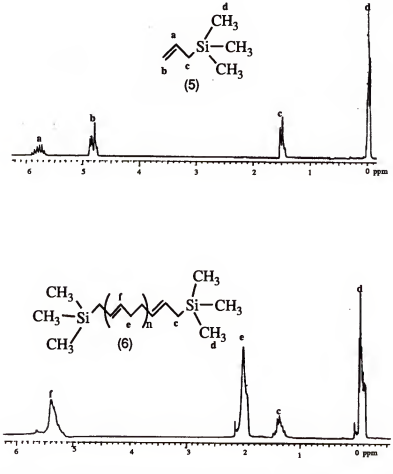


Figure 3.8. ^1H NMR of allyltrimethylsilane (5) (above) and the resultant α,ω-bis(trimethylsilyl)-1,4-polybutadiene (6) where n = 2, 3 and 4.

^{1}H NMR results display the incorporation of allyltrimethylsilane into the backbone of polybutadiene, but the degree of depolymerization and the dispersity of the polymer are still unknown. However in Figure 3.9, gel permeation chromatography (GPC) data for the polymer and oligomers clearly demonstrate the clean depolymerization of high molecular weight 1,4-polybutadiene (M_n=87,000) to oligomers of polybutadiene (M_n=335).

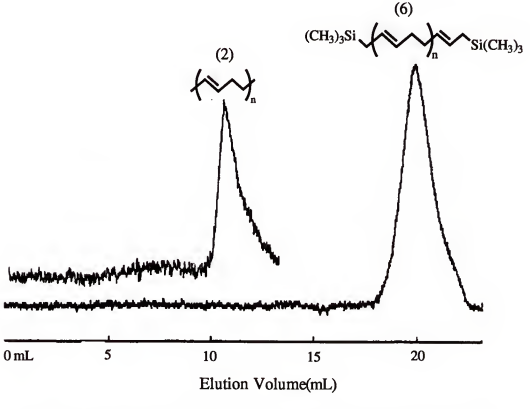


Figure 3.9. Gel permeation chromatography of 1,4-polybutadiene (2) and the resultant α,ω-bis(trimethylsilyl)-1,4-polybutadiene (6) where n = 2, 3 and 4.

Moreover, three gas chromatography / mass spectral (GC/MS) traces (Figure 3.10) unequivocally show that perfectly difunctional telechelic oligomers have been synthesized by this chemistry. Note that the peaks in Figure 3.10 are GC peaks with attached mass labels obtained from the mass spectra. The top GC trace displays a perfectly difunctional oligomer with a mass of 308 which

corresponds to two units of polybutadiene found between trimethylsilyl endgroups. The two GC traces that follow both represent telechelics with a functionality equaled to 2.0 which have three (m/e 362) and four (m/e 416) polybutadiene units, respectively. No other products are present in this reaction mixture. Each of the three traces show more than one peak present, which reflects the presence of isomers for each telechelic oligomer. Most likely, these are geometric isomers of polybutadiene.

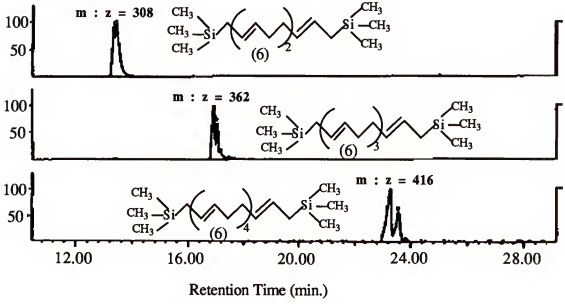


Figure 3.10. Gas chromatograph with mass labels obtained from mass spectra of the resulting α,ω-bis(trimethylsilyl)-1,4-polybutadiene (6) where n = 2, 3 and 4.

Allyltrimethylsilane Depolymerizing Agent with Molybdenum Catalyst

The molybdenum version of Schrock's alkylidene (catalyst 2) also has been used to depolymerize 1,4-polybutadiene (2). Catalyst 2 was reacted under identical conditions to the depolymerization of polybutadiene with catalyst 1 and resulted in the formation of perfectly difunctional α,ω-bis(trimethylsilyl)-1,4-polybutadiene oligomers (7) where n = 1 and 2 (Figure

3.6). The mass spectral data shown in Figure 3.11 clearly illustrates the synthesis of two telechelic oligomers with corresponding masses of 308 and 362. Since the mass spectral data were obtained from chemical ionization, the m^{+1} peak is represented in the spectra instead of the molecular ion peak (m).

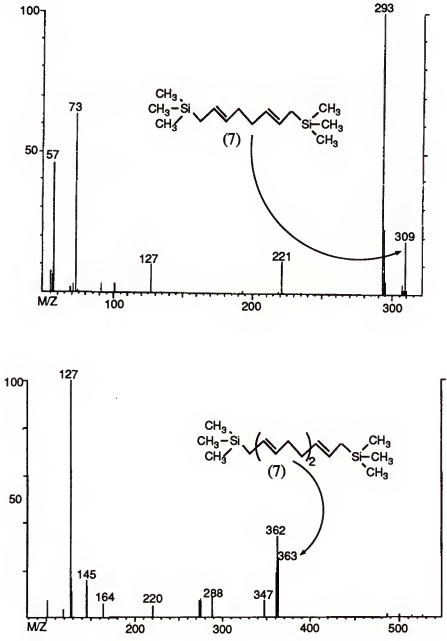


Figure 3.11. Mass spectra of α,ω-bis(trimethylsilyl)-1,4-polybutadiene (7) where n = 1 and 2.

A possible explanation for the increased depolymerization conversion with the molybdenum catalyst may be attributed to the kinetic advantage the molybdenum catalyst offers over the tungsten catalyst. Patton reported that in the polymerization of 1,9-decadiene the molybdenum catalyst produced an oligomer, with a Dp = 11, approximately 40 times faster than the corresponding tungsten catalyst.[169]

Thus far this chemistry exclusively produces trimethylsilyl terminated macromolecules, which are not telechelics in the true sense of the word. A telechelic is defined as a molecule with reactive functionality at the α- and ω-positions. However a reactive functional group can be placed at the termini upon reaction of the allyl silated end groups with an electrophile thereby generating a tetrasubstituted telechelic (Figure 3.12).[170] Depending on the electrophile employed; primary, secondary or tertiary alcohols can be generated along with the vinyl groups. Since the functionalities found in these telechelics can be selectively reacted, one functional group could be used as a monomer while the other would be available for crosslinking.

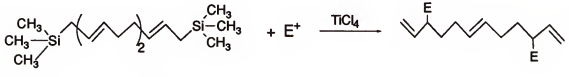


Figure 3.12. Proposed reaction to generate reactive endgroups on α,ω-bis(trimethylsilyl)-1,4-polybutadiene (E+ = formaldehyde, acetaldehyde, acetone).

Allylchlorodimethylsilane Depolymerizing Agent

Following this study, a more reactive depolymerizing agent was employed to further demonstrate the potential for this depolymerization scheme.

Allylchlorodimethylsilane was chosen to see if the labile silicon chlorine bond would react with the molybdenum alkylidene. Previous work published by Streck reported the use of allylchlorodimethylsilane as a chain transfer agent in the molecular weight control of poly(1-pentenylene).[114] The molecular weight control was very efficient, and there was no apparent dissociation of the silicon chlorine bond in the presence of the classical catalyst system (WCl_6 / $SnBu_4$). With this information, allylchlorodimethylsilane (8) was employed in the depolymerization of 1,4-polybutadiene (Figure 3.7) with the molybdenum catalyst. The polybutadiene was quantitatively depolymerized to the perfectly difunctionalized monomer, α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (9), according to GC/MS techniques (Figure 3.13).

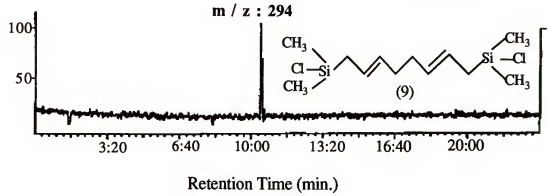


Figure 3.13. Gas chromatograph with mass labels obtained from mass spectrum of the resulting α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (9)

The ^1H NMR also illustrates the clean synthesis of α,ω-bis(chlorodimethylsilyl)-1,4-polybutadiene (9). As shown in Figure 3.14, the integration of the proton resonances corresponding to the butadiene methylenes (2.05 ppm), allyl methylenes (2.20 ppm), and vinyl protons (5.60) all represent four protons which correlate to the structure α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (9). This, in fact, is the only

depolymerization to date that has resulted in quantitative conversion to the monomeric unit, n = 1.

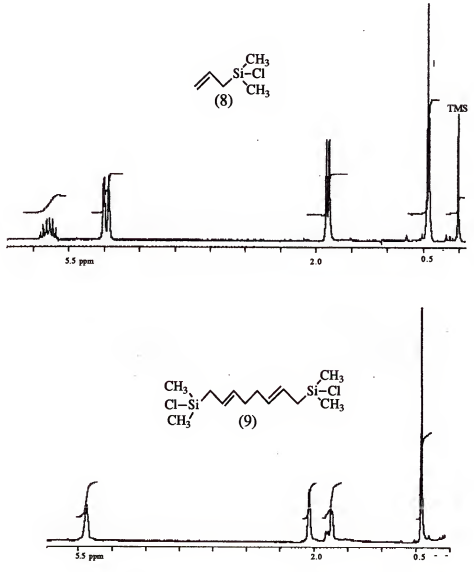


Figure 3.13. ^{1}H NMR of allylchlorodimethylsilane (8) (above) and the resultant telechelic α,ω-bis(chlorodimethylsilyl)octa-2,6-diene (9).

Conclusions

The employment of functionalized depolymerizing agents has advanced ADMET depolymerization chemistry, permitting the formation of perfectly difunctional telechelic oligomers with reactive endgroups i.e. allylchlorodimethylsilane. Futhermore, with the advent of the molybdenum catalyst, depolymerization chemistry is accelerated whereby lower molecular weight telechelics are synthesized more efficiently. As will be illustrated in the following chapters, the molybdenum catalyst's increased tolerance toward functionality permits the use of heteroatom containing depolymerizing agents.

CHAPTER 4

SYNTHESIS OF ESTER , SILYL ETHER, AND IMIDE TELECHELIC POLYBUTADIENE OLIGOMERS

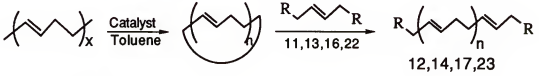
Preparing telechelics with perfect difunctionality (f=2.0) has been a challenge for years. Many methods have been investigated, including step growth,[4,5,8,9] anionic,[19-21,23,26,27] cationic,[34-36] and free radical procedures,[38,44,46] and significant progress has been made in this field. In most cases, however, the average functionality of the oligomers is a value other than two.

Recently, the metathesis polymerization of cyclooctadiene with a chain transfer agent has been described as producing telechelic polybutadiene where the functionality was close to 2.0.[119,146] There have also been attempts to produce perfectly difunctional telechelics by metathesis degradation.[21-26] These reactions employ classical catalyst systems such as those based on WCl_6/Lewis acid cocatalyst, and it is evident that these classical systems cause side reactions which decrease the average functionality of the telechelic oligomers.

As reported in chapter 3, the depolymerization of 1,4-polybutadiene yields perfectly difunctional (f=2.0) telechelic polybutadiene oligomers when α,ω-allylsilanes are employed in the ADMET depolymerization scheme. These 2.0 telechelics were synthesized with the well-defined Schrock catalyst,

M(NAr)(CHC(CH$_3$)$_2$Ph)-(OCCH$_3$(CF$_3$)$_2$)$_2$ (M = W[125] or Mo,[127]), and the results prompted us to explore this opportunity more broadly.

The employment of various functionalized depolymerizing agents have been exploited to broaden the scope of ADMET depolymerization chemistry and generate perfectly difunctional α,ω-diester, disilyl ether, and dimide telechelic polybutadiene oligomers (Figure 4.1). The presence of perfect difunctionality is unequivocally shown via mass spectrometry.



11,12 R = $CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

13,14 R = $(CH_2)_2O\overset{O}{\overset{\|}{C}}CH_3$

16,17 R = $CH_2OSi(CH_3)_2C(CH_3)_3$

22,23 R =



Figure 4.1. Depolymerization of 1,4-polybutadiene with ethyl pentenoate (12), pentenyl acetate (14), *t*-butyldimethylsiloxy butene ether (17), and allylphthalimide (23).

A revised mechanism of ADMET depolymerization is illustrated in Figure 4.2, whereby the cyclization of polybutadiene precludes the linear depolymerization. Initially, the precatalyst (a) metathesizes with a functionalized monoene (b) to generate the symmetrical olefin (c) and a new alkylidene (d). Concurrently, intramolecular metathesis of polybutadiene is producing macrocyclic butadiene (e); the new alkylidene (d) and the macrocyclic (e) form a trisubstituted metallocyclobutane which can productively cleave affording a ring opened butadiene oligomer (f) with the catalyst at the α-

position and the functionalized depolymerizing agent at the ω-position. The catalyst exchanges with the symmetrical olefin (c) to produce a difunctional telechelic (g). This mechanism is substantiated by the data presented herein.

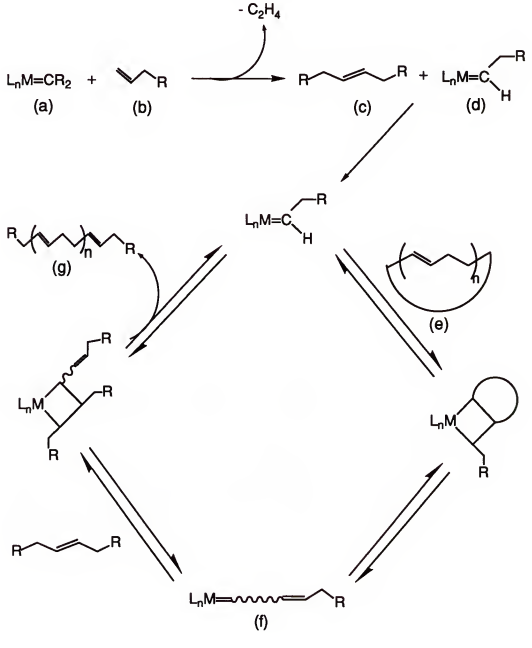


Figure 4.2. Proposed ADMET depolymerization mechanism.

Ester Terminated Telechelics

The synthesis of α,ω-diester polybutadiene telechelics by olefin metathesis were concurrently produced when dimethyl-3-hexenedioate was used as a depolymerizing agent in both the degradation of polybutadiene[115] and the polymerization of cyclooctadiene.[117] In the degradation of 1,4-polybutadiene ($M_n = 10^5$) with WCl_6/Me_4Sn, a prepolymer of butadiene was generated whereby 92% of the polymer was terminated by ester groups (Figure 4.3). The polymerization technique led to a similar degree of functionality which can be attributed to the inefficiency of the classical catalyst.

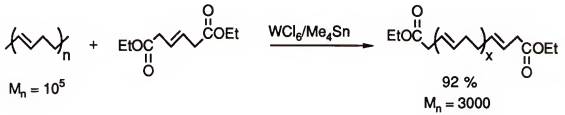


Figure 4.3. Degradation of 1,4-polybutadiene with dimethyl-3-hexenedioate.

Streck's[114] review on metathesis active chain transfer agents illustrates the employment of esters in the molecular weight control of polypentylene. Streck discovered that one methylene spacer must separate the ester from the olefin for productive metathesis to occur. Knowing the limitations of unsaturated esters with a classical catalyst system has allowed for the employment of ethyl pentenoate (12) in the depolymerization of 1,4-polybutadiene (15). The result of which generates perfectly difunctional diester telechelics (Figure 4.1). Ethyl pentenoate was chosen because two methylene spacers separate the olefin from the carbonyl. Unless two or more methylenes are present, the negative neighboring group phenomenon inhibits productive metathesis when Schrock's

molybdenum catalyst is employed,[160] whereas Streck's results with a classical catalyst system only required one methylene spacer. There are two possible explanations for this negative neighboring group phenomenon. First, the electron withdrawing ester may polarize the olefin such that the formation or decomposition of the metallocycles in the catalytic cycle are hindered.[160] Second, the carbonyl may coordinate with the metal center forming ring structures as shown in a similar system.[171] This process competes with productive metathesis, either decreasing the rate of reaction or completely inhibiting the reaction altogether.

Keeping this effect in focus, depolymerization with ethyl pentenoate generates perfectly difunctional telechelic esters (12) with masses of 282 and 336 according to GC/MS techniques (Figure 4.4). These masses correspond to n = 1 and 2 butadiene repeat units. The ratio of n = 1 to 2 is 78:22.

Pentenyl acetate was also used in the depolymerization of 1,4-polybutadiene. Since three methylene spacers separate the heteroatom from the olefin, productive metathesis occurred generating the α,ω-diacetate polybutadiene telechelic (14) (Figure 4.1). The GC/MS data indicates that there are two GC peaks which correspond to n = 1 and 2 butadiene repeat units. The ratio of n = 1 to 2 is 78:22. The masses of the two telechelics are 282 and 336 respectively, which is identical to its empirical equivalent α,ω-bis(ethoxycarbonyl)-1,4-polybutadiene (12).

As shown in Figure 4.5, the mass spectra of α,ω-bis(ethoxycarbonyl)-3,7-decadiene and α,ω-bis(acetoxy)-4,8-dodecadiene can be differentiated by their distinct fragmentation patterns. In the above mass spectrum, α,ω-bis(ethoxycarbonyl)-3,7-decadiene's first fragmentation occurs with the loss of ethoxy, followed by the loss of a second ethoxy group.

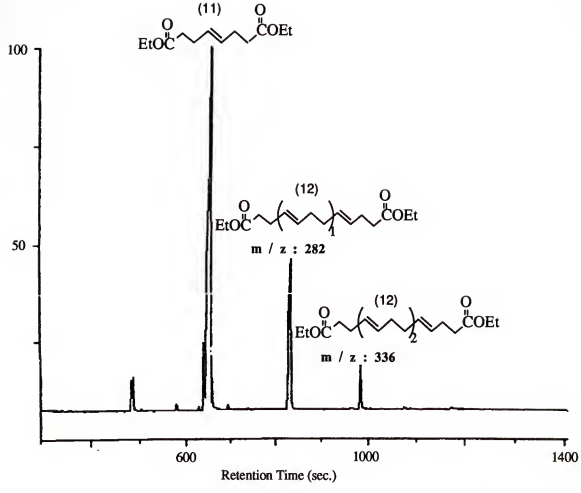


Figure 4.4. Gas chromatograph with mass labels obtained from mass spectrum of bis(ethoxycarbonyl)-1,4-polybutadiene (12).

On the other hand, α,ω-bis(acetoxy)-4,8-dodecadiene's fragmentation begins with the loss of one acetoxy group followed by the loss of the other acetoxy. It should be noted that the mass spectra were obtained by chemical ionization methods, which resulted in producing an intense M^{+1} (quasimolecular ion) peak of 283. The mass spectra of α,ω-bis(ethoxycarbonyl)-3,7-decadiene has two extraneous peaks at 311 and 323 mass units which can be attributed to the CH_4 induced chemical ionization. This ionization leads to the formation of ionic carbon clusters such as $C_2H_5^+$

and $C_3H_5^+$, resulting in the increase of the quasimolecuar ion peak to 311 and 323 respectively.

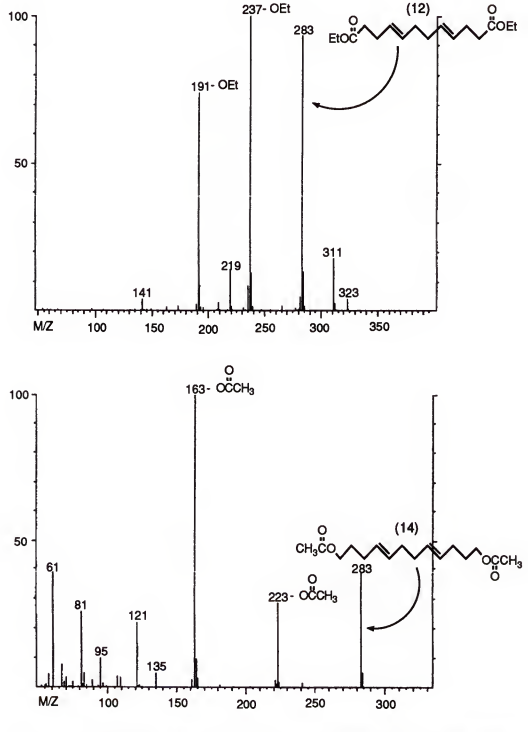


Figure 4.5. Mass spectra of α,ω-bis(ethoxycarbonyl)-3,7-decadiene (12) (above) and α,ω-bis(acetoxy)-4,8-dodecadiene (14).

According to Streck, the esters of fumaric acid and maleic acid were not metathetically active.[115] To verify these results, diethyl fumarate and diethyl maleate were used as depolymerizing agents in the depolymerization of 1,4-polybutadiene with Schrock's molybdenum alkylidene (Figure 4.6). As was expected, the reaction afforded starting material.

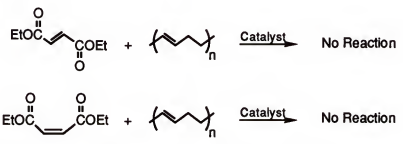


Figure 4.6. Attempted depolymerization of 1,4-polybutadiene with diethyl fumarate (above) and diethyl maleate.

Silyl Ether Terminated Telechelics

Diol functionalized telechelics have been sought for their macromonomer applications in the synthesis of polyurethanes for years.[32] The most widely industrially applied diol telechelic is α,ω-bis(hydroxy)polyoxyethylene because it can be readily synthesized with a functionality = 2.0. The interest in diol telechelics and the ease in which ADMET depolymerization produces perfectly difunctional telechelics has led to the utilization of alcohol depolymerizing agents in the synthesis of α,ω-bis(hydroxy)-1,4-polybutadiene. Initially these reactions failed, most likely because the alcohol functionality decomposes the active catalytic species. Consequently, the alcohol must be protected. As shown in Figure 4.1 *t*-butyldimethylsiloxy butene ether (16) was reacted with 1,4-polybutadiene (15) and the molybdenum catalyst, producing 2.0 telechelics (17), where n = 1 and 2 with a 81:19 ratio. Further addition of catalyst and

depolymerizing agent does not alter the product ratio. Nonetheless, gel permeation chromatography (GPC) data (Figure 4.7) demonstrate the complete conversion of high molecular weight 1,4-polybutadiene to telechelic oligomers of polybutadiene. No cyclics were observed in this case.

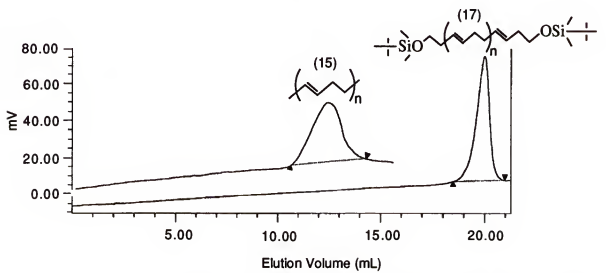


Figure 4.7. Gel permeation chromatograph of 1,4-polybutadiene (15) and resulting telechelics (17) where n = 1 and 2.

On the other hand, the chemistry illustrated in Figure 4.8 shows the depolymerization of 1,4-polybutadiene (15) with bis(*t*-butyldimethylsilyl)-2-butene ether (18) yields telechelic oligomers (n = 1 and 2) and macrocyclic polybutadiene (z = 4 and 5) (19). The ratio of telechelic to macrocylic was 88:12. The gas chromatography/mass spectral data is shown in Figure 4.9. The formation of macrocyclics can be attributed to the negative neighboring group effect where the oxygen β to the alkylidene causes a competitive decomposition of the alkylidene before all macrocyclics can be quantitatively converted to the telechelic. Decomposition of the catalyst, caused by the β oxygen, has also been shown in the polymerization of telechelic polybutadiene.[146]

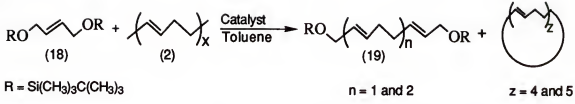


Figure 4.8. Depolymerization of 1,4-polybutadiene (2) with bis(*t*-butyldimethylsilyl)-2-butene ether (18).

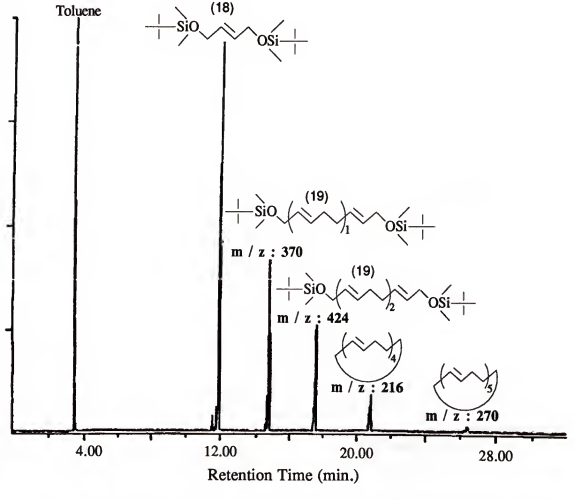


Figure 4.9. Gas chromatograph with mass labels obtained from mass spectra of the resulting α,ω-bis(t-butyldimethylsiloxy)-1,4-polybutadiene (19) where n = 1 and 2 and macrocyclic butadiene where n = 4 and 5.

Earlier work with a classical catalyst system has shown that intramolecular cyclization can preclude the formation of linear telechelics. For example, Calderon *et al.* found that intramolecular metathesis degradation of polybutadiene yielded macrocyclics of 3 to 8 repeat units.[172] This process is accelerated if the initial concentration of the polybutadiene is below the equilibrium concentration ("equilibrium concentration" is defined as the maximum concentration of polymer at which there is quantitative conversion of linear polymer to macrocyclics). If the concentration of polybutadiene is higher than the equilibrium concentration, then the polymer undergoes partial degradation yielding macrocyclic oligomers and residual high molecular weight linear polymer. Although the equilibrium concentration has not been determined for toluene, the polybutadiene equilibrium concentration is 0.65 M in chlorobenzene at 30°C.[173]

To prove that cyclization occurs under ADMET conditions, a reaction analogous to Calderon's was attempted, except the molybdenum alkylidene was used instead of a classical catalyst system. Figure 4.10 illustrates generation of macrocyclics (20) when a 0.48 M polybutadiene (15) solution in toluene was exposed to the molybdenum catalyst. As shown in ^{1}H NMR (Figure 4.7) , the macrocyclics have a vinylic proton resonance at 5.40 ppm, a shift from the vinylic protons of polybutadiene (5.75 ppm). The GC trace has nine peaks which represent macrocyclic trimer and tetramer regioisomers, and these data suggest that the depolymerization mechanism proceeds first through a competitive intramolecular formation of macrocyclics, and followed by cross metathesis with the depolymerizing agent to form telechelics.

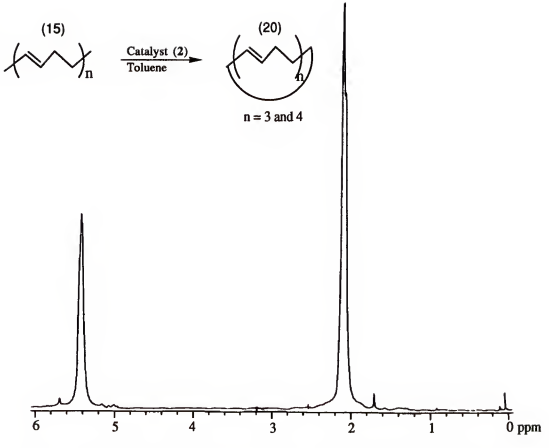


Figure 4.10. ^{1}H NMR of the resulting macrocyclic butadiene (20).

Imide Terminated Telechelics

There are few successful routes in synthesizing primary amine terminated polybutadiene telechelics. One successful attempt was the free radical polymerization in which azoisobutyronitrile (AIBN) initiated and terminated the propagating chain, resulting in a α,ω-bis(cyano)polybutadiene telechelic (Figure 4.11).[174] The cyano endgroups are then reduced upon addition of dibutylaluminumhydride, thereby affording a primary amine telechelic with a functionality of 1.8 to 1.9. The microstructure of the polymer is typical for a radical polymerization: 75% 1,4 and 25% 1,2.

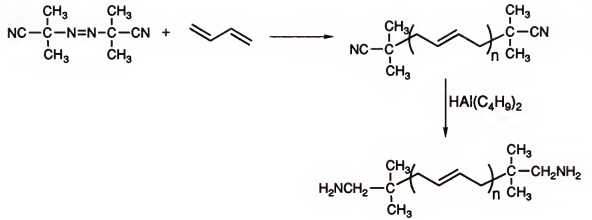


Figure 4.11. Free radical polymerization of α,ω-diaminopolybutadiene.

To obviate any 1,2 addition, ADMET depolymerization chemistry was employed with a protected primary amine. As illustrated in Figure 4.1, polybutadiene (15) was depolymerized with allylphthalimide (22) and catalyst 2, affording imide functionalized telechelics (23), where n = 1 and 2 with a 79:21 ratio by GC/MS techniques (Figure 4.12). Depolymerization occurred quantitatively to the telechelics, even though one methylene spacer separated the nitrogen from the olefin. We believe coordination of the nitrogen was minimized by using an imide functionality, which sterically encumbers the nitrogen lone pair, thereby obviating the negative neighboring group effect.

In order to study this "β nitrogen" phenomenon further, a secondary acyclic amine, N-(*t*-butoxycarbonyl)allylamine (24), was reacted with the molybdenum catalyst in a NMR scale reaction (Figure 4.13). Productive metathesis was observed. Initially, the ^{1}H NMR spectrum displayed a molybdenum alkylidene at 12.4 ppm., a compound which results from the exchange of molybdenum neophylidene with N-(*t*-butoxycarbonyl)allylamine to produce an amide alkylidene (a) (s,12.4 ppm.) and 3-methyl-3-phenylbutene (b) (dd,6.1 ppm). After 1.5 h, there was no change in the size of the alkylidene

peak and an internal olefin peak appeared at 5.4 ppm corresponding to a 20% conversion to the bis(N,N-(*t*-butoxycarbonyl)amino)-2-butene (25). An ethylene peak (f) was also present at 5.20 ppm, further suggesting that dimerization occurred. After 8 h, the alkylidene peak completely disappeared, resulting in only a 60% conversion to dimer. Unlike the imide reaction, these observations suggest that coordination competes with dimerization.

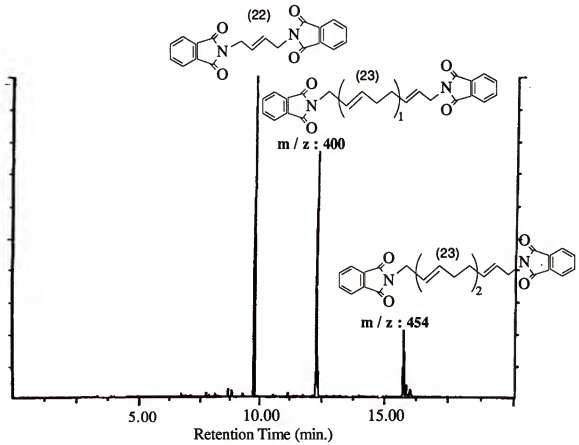


Figure 4.12. Gas chromatograph with mass labels obtained from mass spectra of the resulting α,ω-bis(phthalimide)-1,4-polybutadiene (23) where n = 1 and 2.

N-(*t*-butoxycarbonyl)allylamine (26) was employed in the attempted depolymerization of polybutadiene, but no productive depolymerization occurred. From this result, we hypothesize that coordination of the nitrogen or

carbonyl with the metal center is competing with productive depolymerization of 1,4-polybutadiene. The competing coordination slows the reaction and ultimately, as in the case of the NMR reaction, decomposes the alkylidene.

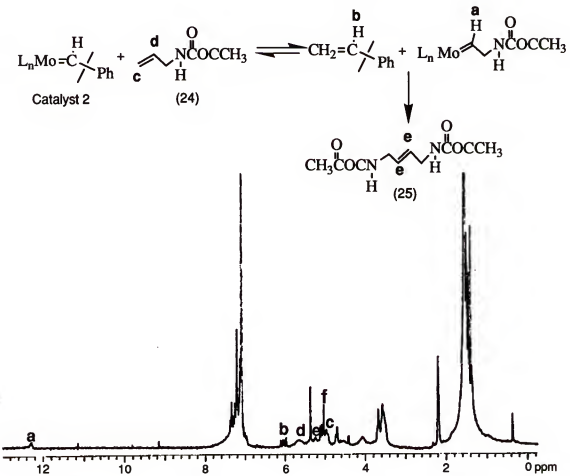


Figure 4.13. ^{1}H NMR of the reaction mixture in the dimerization of N-(*t*-butoxycarbonyl)-allylamine (25) after 1.5 h.

Protected Allylalcohol Depolymerizing Agents

A major goal in this research is to obviate the negative neighboring group effect. As mentioned earlier, allylphthalimide (22) depolymerizes polybutadiene even though nitrogen is one methylene spacer from the alkylidene. These data suggest that protected allylalcohol depolymerizing

agents might be synthesized with structures similar to allylphthalimide such that coordination of the oxygen with the alkylidene is minimized.

Two protected allylic alcohols have been purchased whereby the oxygen of the alcohol is tied back in a ring structure similar to that of the nitrogen in allylphthalimide. Both 4,7-dihydro-1,3-dioxepin (Aldrich) and 4,7-dihydro-2-phenyl-1,3-dioxepin (Aldrich) are 2-butene-1,4-diols protected with formaldehyde and benzaldehyde respectively. Since the alcohol is protected in the form of a cyclic, depolymerization will not take place when cross metathesis occurs between the polymer and the cyclic acetal. Instead, cross metathesis will generate a random copolymer with butadiene and acetal repeat units. The number of butadiene units which separate each acetal unit will depend on the degree of incorporation of the acetal. Once incorporated, the acetal can be converted to the alcohol under acidic conditions, producing α,ω-bis(hydroxy)-1,4-polybutadiene (Figure 4.14).

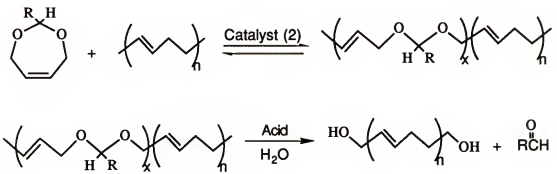


Figure 4.14. Proposed synthesis of α,ω-bis(hydroxy)-1,4-polybutadiene where R = H or Ph.

Attempts at this chemistry have proven unsuccessful and we feel the problem originates from the inability of the cyclic acetal to ring open. Even when the substituent is changed from a hydrogen to a phenyl group, there is not enough ring strain generated for ring-opening cross metathesis to occur. This

led to a more fundamental study to see if the cyclic acetals would homopolymerize in a NMR scale reaction in deuterated benzene or in the bulk. Both 4,7-dihydro-1,3-dioxepin and 4,7-dihydro-2-phenyl-1,3-dioxepin did not ring-open in either the NMR reaction or in the bulk. The ^{1}H NMR reaction showed no shift in the alkylidene proton resonance and the alkylidene resonance appeared for over 3 h, leading us to believe that the catalyst was not decomposing.

One possible explanation revolves around the absence of sufficient ring strain in the molecule. ROMP is typically enthalpy driven with the release of ring strain in 3- and 4-membered rings and non-bonded strain for 8-, 9- and 10-membered rings resulting from intra-ring interactions. The polymerizability of 7-membered rings is largely dependent upon reaction conditions, since the magnitude of enthalpy and entropy terms are very similar. Thus, 7-membered cyclic acetals may not have a sufficient thermodynamic driving force to form polymer.

Conclusions

ADMET depolymerization chemistry is a viable route in the synthesis of perfectly difunctional (f=2.0) telechelic 1,4-polybutadiene oligomers. Telechelic diesters and disilyl ethers can be synthesized if two methylene spacers separate the olefin from the carbonyl or ether functionalities respectively.

The depolymerization mechanism has been elucidated whereby the reaction initially proceeds through macrocyclic butadienes which then ring open to form telechelic oligomers.

Allylphthalimide can be used as a depolymerizing agent even though a nitrogen is β to the olefin. Apparently, coordination of the imide nitrogen is

minimized, thereby allowing quantitative conversion of polybutadiene to the telechelics. By comparison, the less sterically encumbered N-(*t*-butoxycarbonyl)allylamine metathesizes at a much slower rate, due to increased coordination, resulting in alkylidene decomposition.

The employment of a cyclic acetal in the cross metathesis of 1,4-polybutadiene would be a viable route in incorporating a protected allylic alcohol into the backbone of 1,4-polybutadiene. Thereafter, the copolymer could be reacted with acid to form α,ω-bis(hydroxy)-1,4-polybutadiene. However, neither 4,7-dihydro-1,3-dioxepin or 4,7-dihydro-2-phenyl-1,3-dioxepin had enough ring strain to cross metathesize with 1,4-polybutadiene.

CHAPTER 5

SYNTHESIS OF HIGH MOLECULAR WEIGHT TELECHELICS

Low molecular weight, perfectly difunctional (f=2.0) polybutadiene telechelics have been synthesized previously via ADMET depolymerization whereby the α,ω-positions are terminated by silanes, esters, silyl ethers, and imides (Figure 5.1).

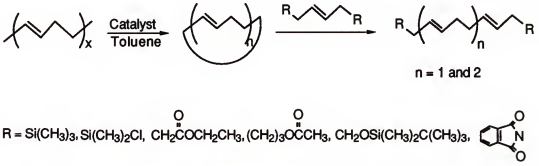


Figure 5.1. Synthesis of perfectly difunctional (f=2.0) telechelic polybutadiene oligomers via ADMET depolymerization.

While this chemistry generates telechelics with one and two repeat units, practical applications demand higher molecular weight. For instance, f < 2.0 polybutadiene telechelics with molecular weights ranging in the thousands are used as monomers in the synthesis of segmented copolymers, such that the molar mass of the polybutadiene segment is large enough to induce phase separation.[3] This chapter demonstrates the synthesis of high molecular weight polybutadiene telechelics via ADMET depolymerization chemistry.

Our first attempt to synthesize higher molecular weight telechelic polybutadiene began with the depolymerization of a 0.13 M solution of 1,4-polybutadiene in toluene using the depolymerizing agent bis(*t*-butyldimethylsiloxy)-3-hexene and catalyst 2. In theory, the number of butadiene repeat units desired in the telechelic should be equivalent to the stoichiometric ratio of $[M_p]/[M_{da}]$; where M_p = moles of butadiene repeat units and M_{da} = moles of depolymerizing agent. In the above reaction, $[M_p]/[M_{da}] = 30$, produces a telechelic with 30 butadiene repeat units if and only if linear depolymerization is the sole reaction taking place. In fact, the attempted depolymerization yielded telechelics with molecular weights ranging from 10^2-10^5 (35).

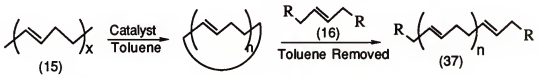
Recognizing that intramolecular cyclization competes with linear depolymerization (thereby establishing a polymer-cyclic equilibrium) has led to a better understanding of how to produce higher molecular weight telechelics. The key is to react the depolymerizing agent, polymer, and catalyst in the bulk, a situation which excludes or limits intramolecular cyclization. It has been shown previously that as the reaction becomes more concentrated the amount of cyclic produced diminishes.[173] Thus bulk polymerization clearly is preferred.

Therefore a bulk ADMET depolymerization of 1,4-polybutadiene was attempted using bis(t-butyldimethylsiloxy)-3-hexene as the depolymerizing agent in a one pot reaction over a period of 48 h. Due to the heterogeneous nature of the catalyst and polybutadiene mixture, our attempt did not show any productive metathesis. In order to increase the homogeneity of the reaction mixture, the reaction must be run either in solution, or the viscosity of polybutadiene must be decreased. As noted earlier, solution polymerization is not very effective.

These problems can be overcome by first forming macrocyclics of butadiene, which reduces the reaction mixtures viscosity. These macrocyclic

butadienes are then cross metathesized in the bulk with the depolymerizing agent to generate high molecular weight polybutadiene telechelics (Figure 5.2).

To prove the point, 1,4-polybutadiene (M_n > 300,000) was intramolecularly cyclized in toluene to form macrocyclic butadiene. Bis(*t*-butyldimethylsiloxy)-3-hexene (2.2 x 10^{-2} equiv. / polymer repeat unit) was added to the macrocyclics, and toluene was removed *in vacuo* thereby creating bulk reaction conditions (Figure 5.2). The reaction was allowed to stir for 48 h.



R = $CH_2OSi(CH_3)_2C(CH_3)_3$

Figure 5.2. Synthesis of high molecular weight polybutadiene telechelics.

Telechelics with 45 butadiene repeat units were expected to be synthesized since the ratio of polymer repeat unit/depolymerizing agent was 45:1. Gel permeation chromatography displayed in Figure 5.3 shows the resultant telechelic (37) with a M_n = 2600 and a PDI of 1.75, which corresponds to a telechelic with n = 43-44 repeat units.

The ^1H NMR in Figure 4 illustrates the clean synthesis of α,ω-bis(*t*-butyl-dimethylsiloxy)polybutadiene (37) where the proton resonances correspond to the vinylic hydrogens (a) at 5.45 ppm, the methylene hydrogens bonded to the oxygen (c) at 3.55 ppm., polybutadiene methylene hydrogens (b) at 2.05 ppm., t-butyl methyl hydrogens (e) at 0.90 ppm., and silyl methyl hydrogens (d) at 0.00 ppm. ^1H NMR end group analysis determined that the number of butadiene repeat units equals 45-46, which coincides with the results obtained from gel permeation chromatograph.

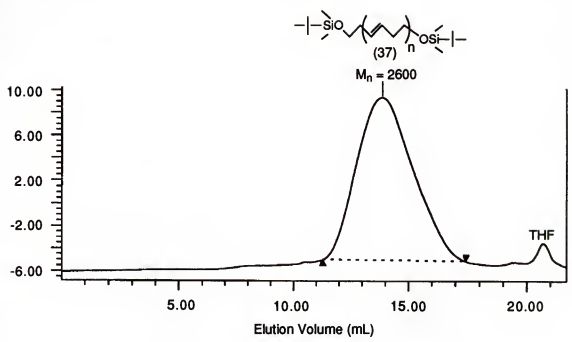


Figure 5.3. Gel permeation chromatograph of α,ω-bis(*t*-butyldimethylsiloxy)-1,4-polybutadiene where n = 43-44.

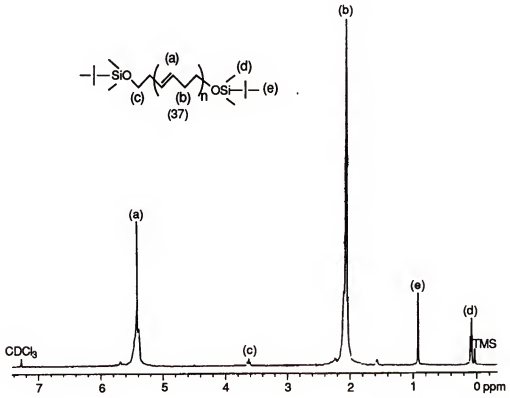


Figure 5.4. ^{1}H NMR of α,ω-bis(*t*-butyldimethylsiloxy)polybutadiene.

A quantitative ^{13}C NMR also demonstrates the synthesis of α,ω-bis(*t*-butyldimethylsiloxy)polybutadiene with 45-46 butadiene repeat units according to end group analysis (M_n = 2700) (Figure 5.5). Also represented in the ^{13}C NMR spectrum is the 80:20 trans/cis ratio which is typical of the thermodynamic equilibrium of a polybutadiene depolymerization.

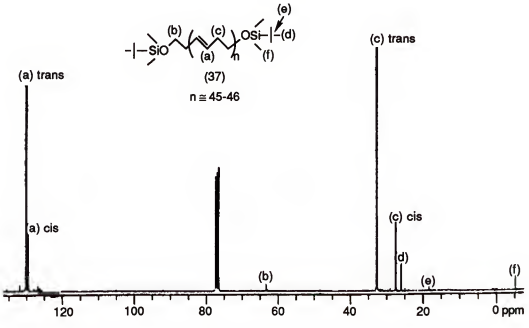


Figure 5.5. Quantitative ^{13}C NMR of α,ω-bis(*t*-butyldimethylsiloxy)polybutadiene.

A reaction similar to the synthesis of α,ω-bis(*t*-butyldimethylsiloxy)polybutadiene was attempted with 5 mg of catalyst 2 instead of 15 mg. The depolymerization was expected to produce telechelics with approximately 30 butadiene repeat units, however, telechelics with 16-17 repeat units were synthesized (36). The reaction products were dissolved in toluene and precipitated in methanol. The toluene/methanol solution was analyzed by gas chromatography (GC), and the GC trace showed a peak which represented the retention time of bis(*t*-butyldimethylsiloxy)-3-hexene. The gel permeation

chromatography data also depicted an incomplete depolymerization. The chromatograph displayed two peaks which represented the resultant telechelic and the macrocyclic butadiene intermediates. This incomplete conversion can be accounted for by the decomposition of catalyst with trace impurities.

ADMET depolymerization is a viable route in the formation of high molecular weight polybutadiene telechelics. The bulk polymerization requirement is met by initially forming macrocyclic butadiene, thereby decreasing the amount of macrocyclic formation. This synthetic scheme is capable of generating well defined, tailored molecular weight polybutadiene telechelics (M_n = 2600).

Depolymerization of Butyl Rubber and Polyisoprene.

The first half of this chapter discussed the formation of high molecular weight polybutadiene telechelics by using a new ADMET depolymerization scheme. Another route in obtaining high molecular weight telechelics is through the depolymerization of block copolymers, such as Kraton™ [poly(styrene-*b*-butadiene)], which forms a high molecular weight styrene telechelic and a functionalized repeat unit of butadiene.[164] This depolymerization successfully produces divinyl terminated butadiene (M_n = 1000) and styrene (M_n = 15400) oligomers when ethylene is used as the depolymerizing agent (Figure 5.6).[164] As discussed in chapter 3, the depolymerization was not quantitative because in the presence of excess ethylene the catalyst forms a stable metallocycle which precipitates, forming white crystals.[168]

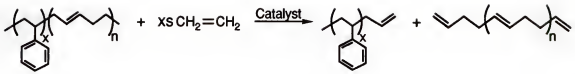


Figure 5.6. Depolymerization of Kraton™ poly(styrene-*b*-butadiene) with an excess of ethylene and catalyst 1.

With the successful depolymerization of Kraton™, the depolymerization of another block copolymer, butyl rubber (isoprene-*b*-isobutylene) was attempted. However, ADMET depolymerization of butyl rubber is more difficult, a phenomenon which can be explained mechanistically. The use of functionalized olefins in the depolymerization of 1,4-polybutadiene produces perfectly difunctional telechelics. The proposed intermediate for this chemistry is a trisubstituted metallocyclobutane which productively cleaves, terminating the polymer chain with the depolymerizing agent, whereas the depolymerization of butyl rubber must proceed through a tetrasubstituted metallocyclobutane. This apparently is a very slow interchange which is evident in the depolymerization of butyl rubber with bis(phthalimido)-2-butene and catalyst 2 in methylene chloride (Figure 5.7).

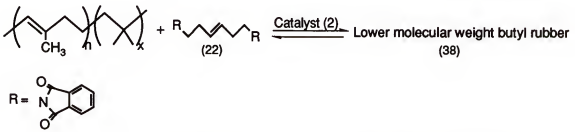


Figure 5.7. Depolymerization of butyl rubber with bis(phthalimido)-2-butene and catalyst 2.

Product 38 of this depolymerization was dissolved in methylene chloride, then precipitated in methanol, and the GPC data (Figure 5.8) for 38 displays a

peak at 11.98 mL. The sample of butyl rubber has an elution volume 10.68 mL, so by comparison it is clear that product 38 is lower in molecular weight. The degree of the depolymerization is very small and is dependent upon the lifetime of the active catalytic species along with the ability to form the sterically hindered tetrasubstituted metallocyclobutane.

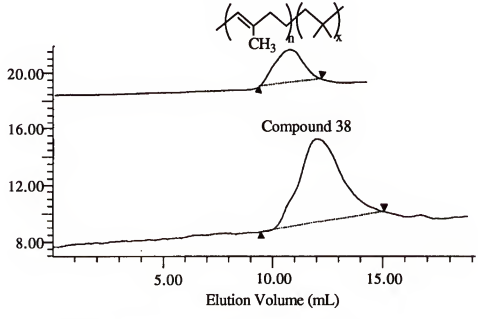


Figure 5.8. Gel permeation chromatography of butyl rubber and the resultant depolymerized product (38).

To further prove that phthalimide is incorporated into the backbone of butyl rubber, the product was analyzed by infrared spectrometry (IR). Illustrated in Figure 5.9, the infrared has two peaks at 1750 cm^{-1} and 1720 cm^{-1}, which represents the imide's carbonyl asymmetric and symmetric stretching vibrations. Also, elemental analysis showed that the polymer contained 1.07 % nitrogen.

The inherent complications in forming the tetrasubstituted metallocycles have ultimately resulted in the failed depolymerization of butyl rubber when *t*-butyldimethylsilyl butene ether (16) is employed (39) (Figure 5.10). In the ADMET depolymerization of butyl rubber, the attack of the depolymerizing agent

occurs at the olefinic site of the unsaturated polymer segment (polyisoprene). Therefore, to gain further insight about the depolymerization of butyl rubber, the depolymerization of polyisoprene was attempted with *t*-butyldimethylsilyl butene ether (16) and catalyst 2 (40); the reaction yielded starting material (Figure 5.10).

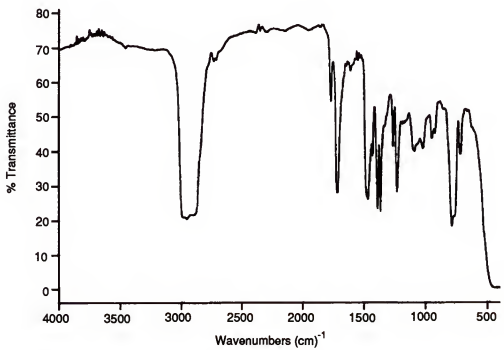
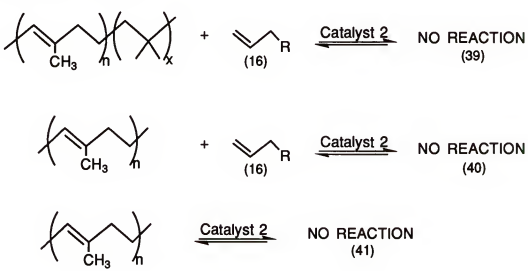


Figure 5.9. Infrared spectrum of the resultant telechelic (38).

The formation of macrocyclic polyisoprene was also attempted by reacting polyisoprene with catalyst in toluene, and again the reaction generated starting material (41) (Figure 5.10). Furthermore, a NMR scale intramolecular cyclization of polyisoprene was attempted with catalyst 2 in deuterated benzene (42). The ^{1}H NMR was analyzed over a 24 hour period to determine if exchange had occurred between the catalyst and polyisoprene. There was no shift in the alkylidene's proton resonance, therefore exchange or formation of a stabilized metallocycle had not occurred.

Previously published results showed that the degradation of polyisoprene was unsuccessful due to a short lived catalyst system.[93] A more stable catalyst system, $W[OCH(CH_2)Cl)_2]_2Cl_4$-$AlEt_2Cl$-anisole, was employed and allowed to react for 10 days. This reaction resulted in the degradation of polyisoprene from a molecular weight of 10^6 to approximately 2.0 x 10^4.[94] However, along with the decreased molecular weight, there was also a loss of unsaturation caused by cationic side reactions derived from the ill-defined classical catalyst system.



R = $CH_2OSi(CH_3)_2C(CH_3)_3$

Figure 5.10. Attempted depolymerization of butyl rubber (above) and polyisoprene (middle) with *t*-butyldimethylsilyl butene ether. Attempted intramolecular cyclization of polyisoprene (below).

While the variability associated with these experiments is not understood, a possible explanation might be found in the work of Konzelman.[175] Konzelman was able to demonstrate that the position of substituents on hydrocarbon dienes can influence olefin metathesis reactivity. For example, hydrocarbon dienes containing 1,1-disubstituted olefins do not polymerize,

since these dienes must proceed through an unfavorable tetrasubstituted metallocyclobutane. On the other hand, when 2-methyl-1,5-hexadiene was polymerized, the reaction proceeded through a trisubstituted metallocycle and polyisoprene (M_n = 5000) was synthesized (Figure 5.11).

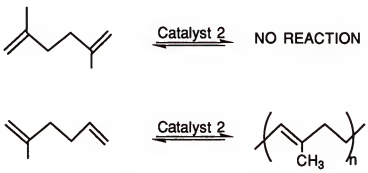


Figure 5.11. Attempted polymerization of 2,5-dimethyl-1,5-hexadiene (above), and polymerization of 2-methyl-1,5-hexadiene (below).

There are two possible reasons why productive metathesis does not occur or occurs very slowly when it proceeds through a tetrasubstituted metallocycle intermediate. First, steric interaction between substituents present on approaching olefins can forbid the formation of the metallocycle. Second, if the metallocycle is formed, the substituents could stabilize the metallocycle, thereby rendering it inactive. According to the ^{1}H NMR reaction of polyisoprene and catalyst, there was no evidence for the formation of the metallocycle.

This steric interaction in the depolymerization of polyisoprene can be overcome by employing a non-functionalized chain transfer agent, ethylene. As discussed earlier, polyisoprene depolymerizes under a 5-6 atm of ethylene pressure at 50°C. In this reaction, the intermediate formed must always be a trisubstituted metallocyclobutane, and for this to occur, the precatalyst must react with ethylene to form 3-methyl-3-phenylbutene and the methylidene (a), the active catalytic species. Unlike the depolymerization of 1,4-polybutadiene,

polyisoprene does not first proceed through the formation of macrocyclics since it would have to form a tetrasubstituted metallocycle. Instead, the methylidene (a) reacts with polyisoprene forming a trisubstituted metallocyclobutane. This productively cleaves, placing an alkylidene (c) and a vinyl group (b) at the terminal positions of the polyisoprene. The alkylidene reacts with ethylene to form another trisubstituted metallocyclobutane, which productively cleaves forming the vinyl terminated polyisoprene (d) and methylidene (a). This process occurs in a catalytic cycle until depolymerization is complete. One final point should be noted. Once the alkylidene is bonded to polyisoprene, cross metathesis with another polymer chain does not occur because it must go through a tetrasubstituted metallocyclobutane. The complete sequence of reactions is fully illustrated in Figure 5.12.

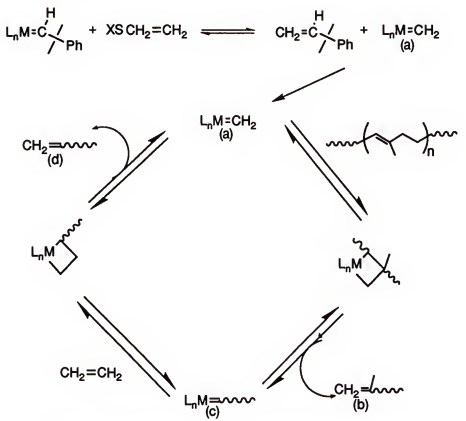


Figure 5.12. Proposed mechanism for the depolymerization of polyisoprene with ethylene.

Conclusions

With the elucidation of the depolymerization mechanism, a new depolymerization reaction scheme was employed in the synthesis of high molecular weight 1,4-polybutadiene telechelics. This new scheme has enabled us to synthesize tailored molecular weight telechelics. In the case illustrated in this chapter, a perfectly difunctional telechelic with a stoichiometric ratio of 45:1, M_p/M_{da}, was synthesized.

The depolymerization of butyl rubber and polyisoprene has proven to be more difficult than that of 1,4-polybutadiene, due to the fact that it must first proceed through a tetrasubstituted metallocycle. A ^1H NMR study of the depolymerization of polyisoprene showed no apparent exchange between the catalyst and polymer over a 24 h period, leading us to believe that if the depolymerization occurs, it does so in a very slow process.

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J. Christopher Marmo was born on May 5, 1968, in Albany, New York. He attended Union College in Schenectady, New York, where he earned a Bachelor of Science degree in chemistry. While attending Union College, he interned for one year at GE Corporate Research and Development in the polymer blends division. He also spent one semester in Florence, Italy, studying Renaissance art history and the Italian language. His graduate school career began in the fall of 1990, and shortly after he decided to join Professor Ken Wagener's research group. He received his Ph.D. in 1994 and began a career as a chemical consultant working for Arthur D. Little in Cambridge, Massachusetts.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kenneth B. Wagener, Chairman
Professor of Chemistry

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as a partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December, 1994

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